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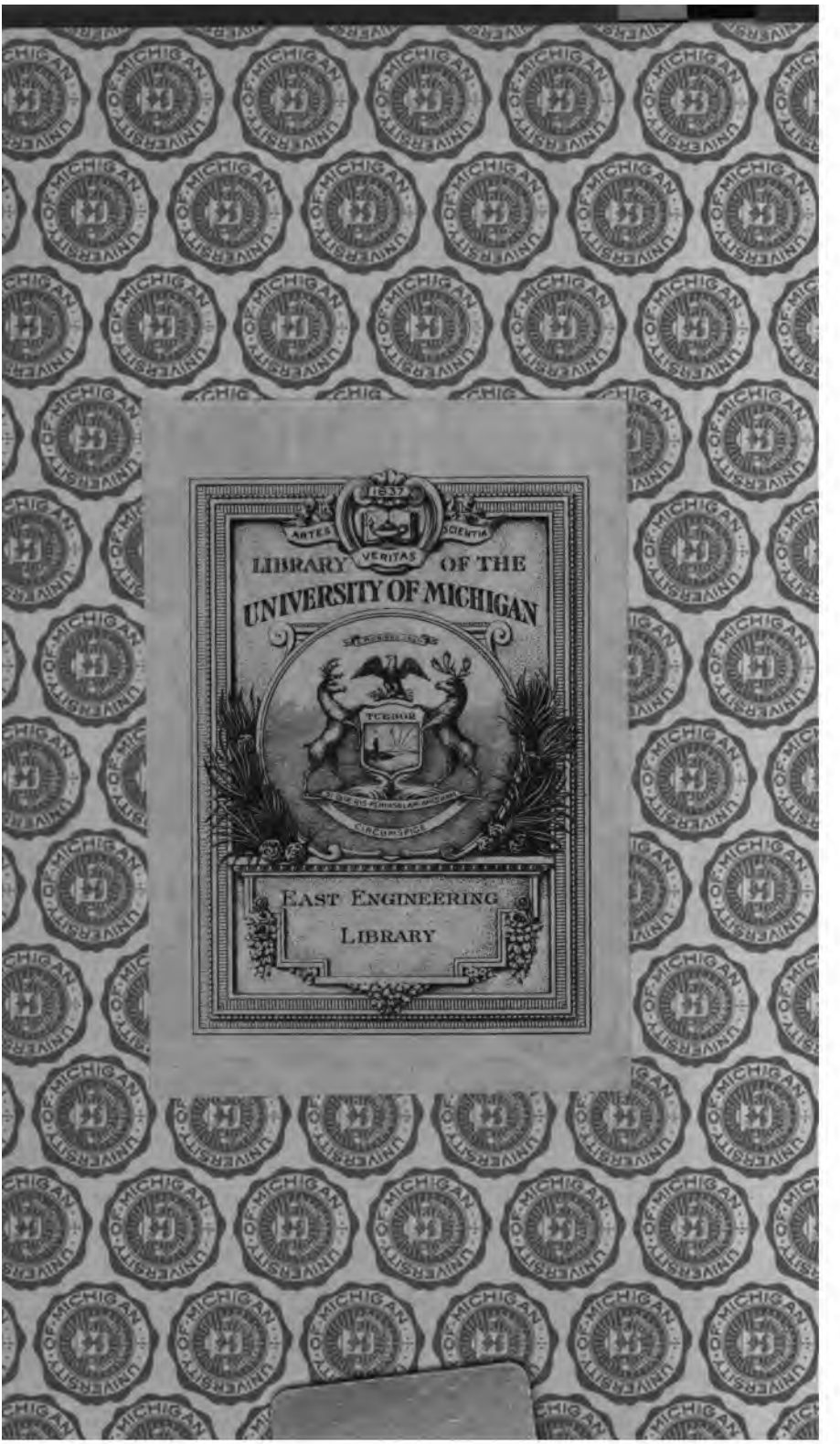
OF THE CHEMISTS OF THE
United States Steel Corporation

FOR THE

SAMPLING AND ANALYSIS
OF

FLUXES, CINDERS, AND REFRACTORIES.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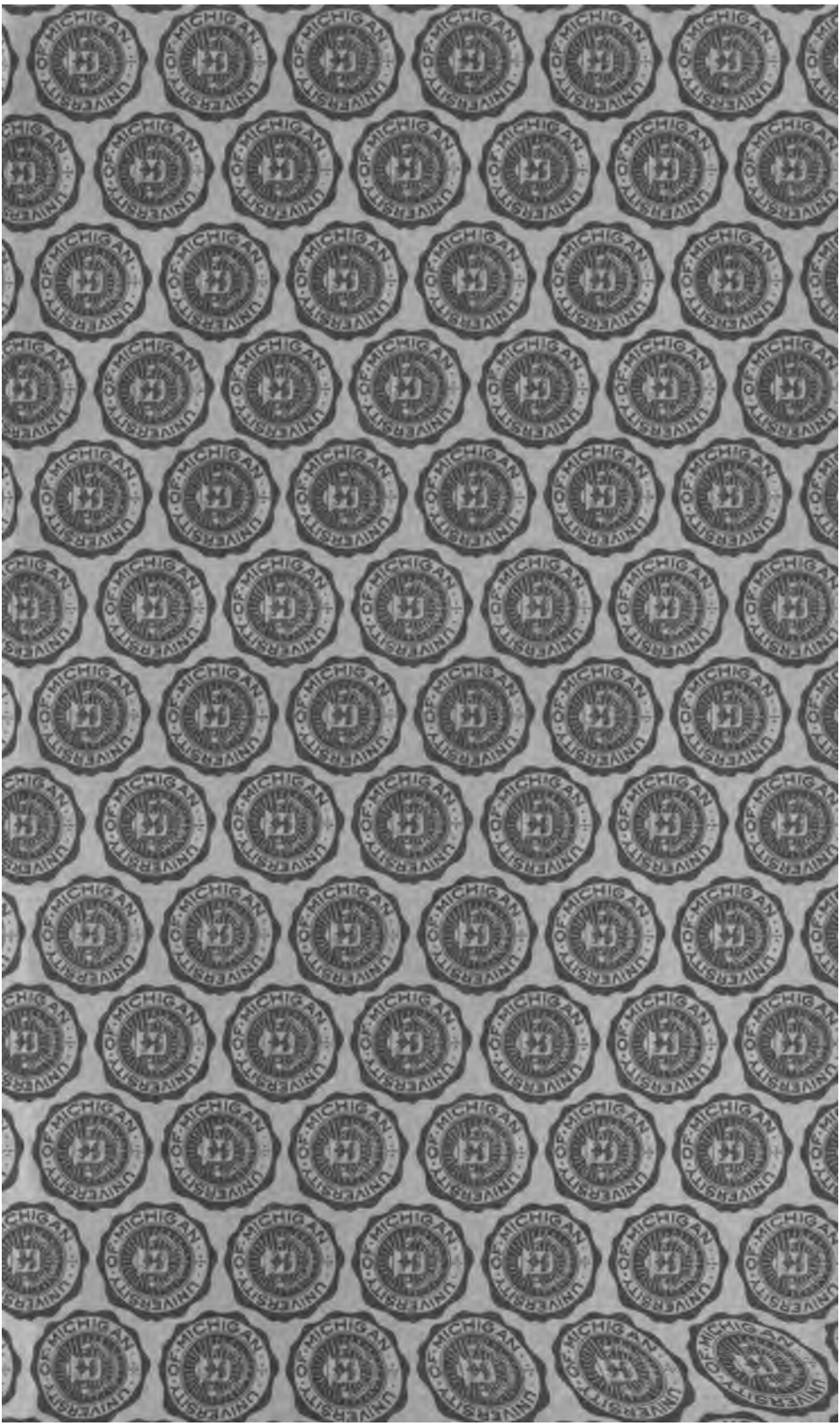
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THE METHODS

OF THE CHEMISTS OF THE

UNITED STATES STEEL CORPORATION

FOR THE

SAMPLING AND ANALYSIS

OF

FLUXES, CINDERS, AND REFRACTORIES

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BY
J. M. CAMP,
CHAIRMAN CHEMIST'S COMMITTEE
UNITED STATES STEEL CORPORATION

PREFACE.

In metallurgical practice, it is desirable that the methods of analysis for all materials, including fluxes, cinders, and refractories, should be rapid and at the same time reasonably accurate. Since the metallurgist must rely largely upon the results of chemical analysis in order to select and dispose of his fluxes and refractories to best advantage, and since the analysis of cinders, or slags, are important factors in controlling metallurgical processes, time is seldom available to the chemist for the painstaking care required to perform an accurate complete analysis. Again, emergencies frequently arise in which the prompt revelation, by the chemist, of the character of such materials as blast furnace slags, which are produced in large quantities and of varying composition, is of the greatest importance. Obviously, such a revelation is possible only when rapid and accurate methods for conducting the analyses are pursued.

To meet these needs and to establish standard methods for the sampling and analysis of these materials, a committee of chemists of the United States Steel Corporation was appointed to select and compile such methods. In performance of its work, this committee made a thorough canvass of the chemists of the Corporation to obtain all methods in vogue at the various laboratories. These methods were classified and critically examined, and those which met with the approval of the committee are presented in this pamphlet on the sampling and analysis of fluxes, cinders, and refractories.

The committee appointed for the preparation of this pamphlet consists of Mr. W. B. N. Hawk, Chief Chemist of the Lorain Works, The National Tube Company, Mr. C. E. Nesbitt, Chief Chemist of the Edgar Thomson Works, Carnegie Steel Company, and Mr. H. E. Campbell, Chief Chemist of the Clairton Works, Carnegie Steel Company.

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METHODS OF SAMPLING.

MOLTEN SLAG SAMPLING.

To meet the requirements aimed for in this pamphlet, any body of slag in the molten state is assumed to be sufficiently uniform in composition to render needless any special precaution for making the sample representative. The sample is dipped from the bath, or from the runner as the slag is being tapped, with a spoon, and chilled by casting into a suitable mould. A small piece is then taken for the analysis, or mixed with additional samples, depending upon the quantity of slag it is desired the analysis should represent.

RAILROAD CAR SAMPLING.

When cinders, raw material, or fabricated refractories are handled in bulk in cars, they are sampled at the surface by the area method. Five points are located in each end of the car, four of them symmetrically placed around the fifth as a center and at a distance from it equal to two-thirds the distance to the sides. Each of these points should represent a definite area equal to one-tenth of the total. If practically all the material is finer than half inch size, the sample is taken with a scoop at the located points; if in large lumps of uniform size, five pieces varying in size from a half inch to a one inch cube are broken with a hammer from different lumps scattered over each of the ten areas; or, if the lumps are small and of suitable size, these may be taken without breaking. If the material contains both lumps and fine, the relative amounts are judged in each area separately, and corresponding amounts of each kind of material are taken therefrom for the sample. These scoopfuls or pieces are combined to form the car sample, and several car samples may be combined in one analytical sample. As a rule, ten is the maximum number of car samples combined in one analytical sample. The weight of the sample varies with the number of cars it represents, but it should not be less than twenty pounds in any case.

When a single carload of very valuable material is to be sampled, the number of points sampled should be increased to thirty or more. The same rule applies to material the quality of which is in question and to material which is known to be lacking in uniformity. In exceptional cases, the car

is sampled during the unloading, and, in this case, care is taken to see that the pieces or scoopfuls are taken from different points in the car corresponding to those designated above.

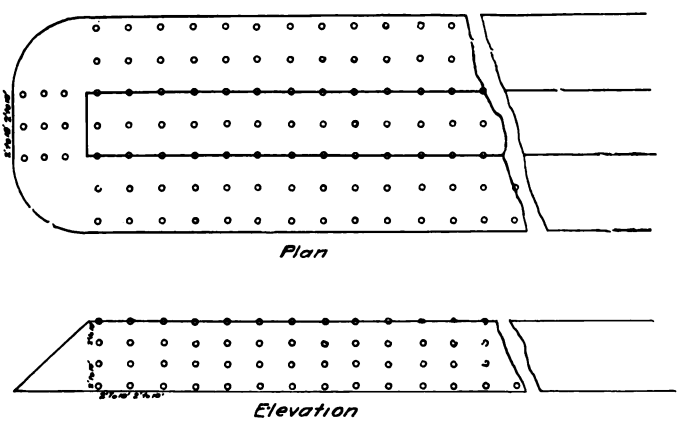
Materials in containers are usually much more valuable than those shipped in bulk, and for this reason special care should be taken to see that the samples are truly representative of the average composition of the materials sampled. In order to secure such a sample, a large number of containers in a shipment should be sampled. In extreme cases, to ascertain if the material sampled is uniform, samples from several different points in each container should be taken and separately analysed.

PILE SAMPLING.

FINE MATERIAL.

The pile is divided as shown in the accompanying diagram by imaginary cross section lines from two to ten feet apart.

STOCKPILE



Starting at one end, two feet from the base, samples are taken along each line from two to ten feet intervals over the entire pile as shown. Each line represents a sample if desired. The ends are sampled in like manner, starting two feet from the base and ending at the top.

LUMP MATERIAL.

In sampling lump material in piles, the knotted rope system, with knots from two to ten feet apart, is used. Beginning at one end, the rope is stretched over the stock pile, and a small portion about one cubic inch in size is chipped from the material which lies directly under each knot. The rope is then moved forward from two to ten feet and the operation repeated until the entire pile is sampled. Each line may be taken as a separate sample or the various lines combined as desired.

CARGO SAMPLING.

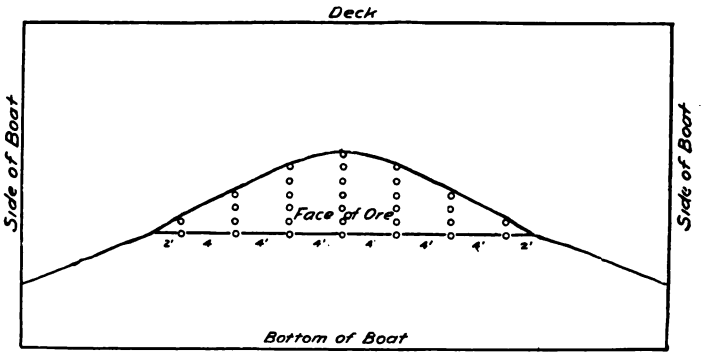
It is difficult to specify a uniform method for sampling cargo shipments because of the different unloading conditions. The boats vary in size and type, and the unloading machines at the various docks differ in number, kind, size, and in the rapidity of their operation. In such cases, the judgment of an experienced sampler must be relied upon to secure a sample that is truly representative of the cargo. However, the following directions are applied in general and may serve as guides to the inexperienced.

FINE MATERIAL.

The general plan is to take portions from the exposed faces of the material while the boat is being unloaded. These portions are obtained by proceeding according to one of two methods, which are described as follows:

FACE METHOD.

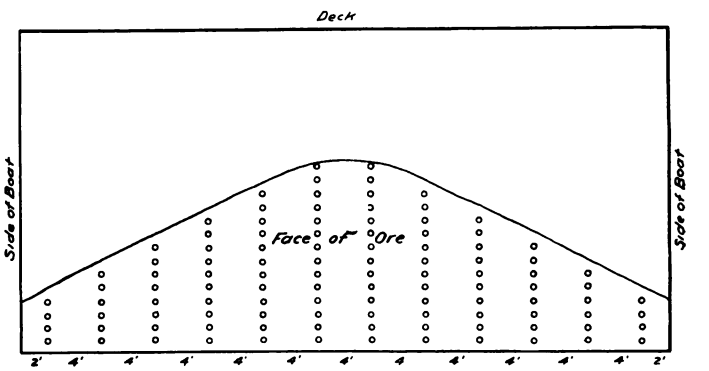
When four to six feet of the material face are exposed by the unloading machine, the sampler enters the hatch and, measuring two feet from the side of the boat or the edge of the face, procures samples at one foot intervals from the bottom to the top of the face. Successive vertical lines are measured four feet apart, and samples are taken as just described. The following diagram is illustrative of the method of sampling the first exposed face of the material:



FIRST SIX FEET OF FACE

This procedure is repeated on the opposite face and is continued in each hatch.

When the bottom of the boat is reached by the unloading machine, thereby exposing new faces, the sampler measures two feet from the side of the boat, and samples are taken at one foot intervals up the exposed face to its top, using a ladder where necessary. The next vertical line is measured four feet from the first line. The samples are taken at one foot intervals on this line as before, and sampling is thus continued across the face. This is repeated on the opposite face of the material, and this procedure continued until the faces of all hatches are sampled, as shown in the following diagram.



FACE TO BOTTOM OF BOAT

CONTINUOUS METHOD.

The aim of this method is to begin sampling as soon as the unloading machines have commenced operation and to continue without intermission until practically the entire cargo is unloaded.

On cargoes up to 4000 tons, when five or six feet of face are exposed by the unloading machine, sampling is commenced at a convenient point at the bottom of the face of the material, and portions are taken two feet apart up the face of the material to the top. Successive vertical lines are measured four feet apart until the starting point is reached, and samples are taken along these lines as just described. The sampler then enters the next hatch from which the material has been partially removed and proceeds to sample it exactly the same way, and thus continues in every hatch. When all hatches are sampled, the sampler begins at the starting point, provided sufficient material has been removed from the hatch since the previous samples were taken to expose fresh faces, and proceeds to secure samples in the same manner as before. This method is continued during the entire time of unloading until less than one-tenth of the cargo is left in the boat.

In order to keep the size of the samples within reasonable bounds and gauge this amount to the size of the boat, procedure is as follows:

On cargoes varying from 4000 to 7500 tons, vertical measurements of two feet are maintained, but the lateral distance between the lines of sampling is increased to six feet. Similarly, for cargoes over 7500 tons, the horizontal distance is increased to eight feet.

LUMP MATERIAL.

Lump material is sampled in the same manner as fine material, either by the face or continuous method, with the exception that the vertical lines are two feet apart instead of four.

In sampling refractory bricks, small pieces are taken from the edges in such a manner as not to interfere with the use of the material. The number sampled is the same as if it were lump material.

Extraneous material, if present in lumpy raw materials, is ignored in taking the sample and made the basis of a separate report.

PREPARATION OF THE SAMPLE FOR ANALYSIS.

MOISTURE DETERMINATION.

From 2 to 50 kilograms of the thoroughly mixed sample are placed in a pan and dried at a temperature not exceeding 105°C. until a constant weight is obtained. The loss in weight multiplied by 100 and divided by the initial weight represents the per cent moisture.

QUARTERING AND GRINDING.

Unless the sample is exceedingly large, the entire amount is crushed to about ¼ inch size before quartering. Following the crushing, the sample is repeatedly mixed and quartered until a portion weighing approximately 200 grams is obtained. This portion is then pulverized to pass through a 100 mesh sieve by grinding it in a hardened steel mortar, by rubbing it between hardened steel plates, or by passing it between hardened steel rolls. If it is desired to avoid the slight contamination of the sample with iron which these tools produce, this grinding is done in agate mortars. In case the material to be analyzed is known to be free of iron or other magnetic substances, the sample may be pulverized with the ordinary grinding equipment, and the major part of the contaminating iron is removed with a magnet. After passing through the 100 mesh sieve, the powder is thoroughly mixed by rolling on glazed paper or shaking in a glass jar, and a suitable amount is retained for analysis. Substances difficult to dissolve or fuse are further ground in an agate mortar. All samples are dried at 100°C. to constant weight previous to beginning the analysis.

SAMPLES CONTAINING METALLIC MATERIAL.

Slags containing metallic particles, or shot, are given a somewhat special and varied treatment, the size of such particles being the chief factor governing the details. In general, the order of operation is as follows: (1) Reduction to as small size as the metallic particles will allow, (2) Quartering to a convenient weight, (3) Weighing the quarter, (4) Magnetic separation. To effect the latter the mass is spread out thinly, and a bar or horseshoe magnet, with a piece of paper folded over the end, is slowly passed through it, when

the magnetic particles, which adhere, are removed. Slag particles, entangled with the magnetic material, are separated by lifting the latter again with the magnet, and any residue is returned to the slag portion. The slag portion is weighed and calculated to the per cent of the quarter from which it came, again crushed or ground, quartered and separated, in the order outlined above as often as necessary or desired, and the final residue is taken for analysis. The numbers which represent the per cent of slag residue in the several quarters are multiplied together; the result is the per cent of slag in the original sample from which the per cent of magnetic material is obtained by difference. The number is used to reduce all of the analytical results to the basis of the original sample, if it is so desired.

Example.

A sample of acid Bessemer slag weighing fifty kilograms is crushed to pass a half inch mesh and quartered to about twenty-five kilograms. Its exact weight is 25.14 kilograms. After taking out all the material which will adhere to the magnet, the residue weighs 22.85 kilograms or 90.89%. This is further crushed to pass an eight mesh, quartered, and weighed. Its weight is 5.42 kilograms and from it 4.82 kilograms of slag are left after magnetic separation, or 88.93%. This is ground to forty mesh, quartered to .784 kilograms and more magnetic material extracted, leaving .746 kilograms or 95.15%. Hence, 95.15% of 88.93% of 90.89% equals 76.91% slag, and the magnetic material by difference equals 23.09%.

When a magnet is applied to a sample in the above manner, metallic iron and magnetic iron oxide, Fe_3O_4, if present, are separated. In blast furnace slags, the magnetic portion consists of iron metal only. Open hearth and converter slags, on the other hand, contain small quantities of magnetic oxide of iron and varying amounts of iron in the metallic state, both of which are attracted by a magnet.

The magnetic portions from blast furnace and open hearth slags are usually discarded since they are very small. Converter slags, however, contain from one to ten per cent and sometimes more of steel metal in the form of shot. Inasmuch as these shot cannot be crushed or otherwise reduced to fineness, the magnetic portion in the original form as separated is taken for analysis. If the amount is too large, the portion is well mixed and quartered until a sample of desired size is obtained.

METHODS OF ANALYSIS.

GENERAL REMARKS.

In the following directions for analysis, it has been the desire to give the methods in considerable detail. In order to avoid constant repetition, however, the following statements are made.

Whenever water is mentioned as a reagent, it is understood to be distilled water. The strength of the acids is indicated by the word concentrated or by the proportion, by volume, of concentrated acid to water in parenthesis. The word concentrated signifies that the ordinary chemically pure acid as received from the manufacturer is used. Ammonia is likewise designated. The specific gravities of concentrated sulphuric, nitric, and hydrochloric acids and ammonia would thus be 1.84, 1.42, 1.19, and .90, respectively. In giving the proportion in parenthesis, the proportion of water is always given last. When per cent is employed to indicate the dilution of a reagent, the numeral expressing the per cent indicates the number of grams of solid or cubic centimeters of liquid added to water to make 100 cc. of solution. It is understood that not only the acids, but all chemicals mentioned are of chemically pure, or C. P., grade. It is recommended that blank analysis be made of all reagents to determine their freedom from impurities that may affect the results of an analysis.

ANALYSIS OF BLAST FURNACE SLAGS.

SILICA.

One-half to one gram of the sample, which need not be ground finer than 100 mesh, is transferred to a platinum or porcelain dish and thoroughly moistened by stirring with a minimum amount of water, after which 20 cc. of concentrated hydrochloric acid are added. The solution may be evaporated rapidly to dryness on a hot plate or over a low gas flame, and the residue baked 10 to 20 minutes at a temperature not exceeding 120°C., or the evaporation may be conducted slowly on a steam bath for at least one hour beyond the time of disappearance of visible moisture, in which case the baking is omitted. Twenty cubic centimeters of water and fifteen cubic centimeters of concentrated hydrochloric acid are added, and heat is applied until the salts are dissolved. The silica is collected on an ashless paper and washed several times with hot dilute hydrochloric acid (1:20) and finally with hot water until free from chlorides. The filtrate and first washings are received in a dish and evaporated. The residue is treated as above, and the recovered silica is removed by means of a new filter. In this case the filter is washed with very dilute cold hydrochloric acid (1:100), when the two precipitates are combined in a platinum crucible and ignited. A few drops of sulphuric acid are added, in order to change all salts to sulphates, and evaporated, when the contents of the crucible are ignited again and weighed. The residue is moistened with water, 3 cc. of concentrated hydrofluoric acid and a few drops of sulphuric acid (1:1) are added, and the solution is evaporated to dryness. The residue is ignited, and the crucible and contents are again weighed. The loss in weight is calculated to per cent silica.

The residue from the silica determination is composed of the oxides of aluminum, iron, and manganese, and possibly titanium. Therefore, if the latter element is present, this residue is fused with a small quantity of sodium carbonate, the fusion is dissolved in a minimum amount of hydrochloric acid (1:1), and the solution is added to the filtrate and combined washings from the silica for the determination of alumina, lime, and other constituents. If there is no titanium present and if the precipitate of the hydroxides in the subsequent operation is to be ignited and weighed, the crucible used in volatilizing the silica is retained, and the precipitated hydroxides are later added and ignited as the total oxides, thus eliminating the fusion of the silica residues.

ALUMINA.

OXIDE METHOD.

The solution for the determination of alumina is brought to a volume of about 200 cc., and about one gram of ammonium persulphate is added. After boiling, a considerable excess of ammonia is added, and the boiling is continued for several minutes. The precipitate, which is composed of the hydroxides of aluminum, iron, and titanium, and the oxide of manganese, is allowed to settle, and the liquid is decanted through a filter. The precipitate is dissolved in dilute nitric acid (1:2) and reprecipitated as before, but in this instance the precipitation is made in the presence of macerated filter paper. The insoluble matter is then collected on a filter and washed with hot water containing a few drops of ammonia until free from any traces of chlorides. The precipitate is strongly ignited and weighed, and a deduction is made for the oxides of iron, manganese, and titanium, or the alumina is separated by the method which follows.

PHOSPHATE METHOD.

The precipitate, after the second precipitation as described above, is dissolved from the filter with hot hydrochloric acid (1:1), after which 400 cc. of cold water and 30 cc. of a ten per cent solution of ammonium phosphate are added. The solution is made just neutral with ammonia, preferably by using methyl orange as an indicator, and then acidified with 1.5 cc. concentrated hydrochloric acid. The solution is stirred until it is clear, 50 cc. of a twenty per cent solution of sodium thiosulphate are added, and the solution is heated to boiling, when 10 cc. of strong acetic acid and 15 cc. of a twenty per cent solution of ammonium acetate are added, and boiling is continued for ten minutes. After the precipitate has settled, it is removed by filtration and washed very thoroughly with hot water. It is then ignited and weighed in a porcelain crucible as aluminum phosphate, 41.84 per cent of which is alumina. If titanium is present in appreciable amount, it is determined as later described, calculated to the phosphate, $Ti_3(PO_4)_4$, and deducted from the weight of the aluminum phosphate. If the sample contains much iron, the precipitation of the aluminum phosphate is repeated by the same procedure before ignition, hot hydrochloric acid (1:1) being used to dissolve the first precipitate from the filter.

The phosphate method may be used to determine the alumina directly in the filtrate from the silica when this solution is not to be used for the determination of other constituents of the slag.

TITANIA.

GRAVIMETRIC METHOD.

The oxide or phosphate residue, remaining from the determination of alumina, is fused with 5 grams of sodium carbonate in a platinum crucible. The fusion is disintegrated in 50 cc. of hot water in a 250 cc. beaker, and the solution is heated to a boiling temperature for ten minutes. The insoluble matter is allowed to settle, and the solution is filtered through a close filter from the sodium titanate and ferric oxide. The residue is washed well with a two per cent solution of sodium carbonate. It may be necessary to refilter the solution, as sodium titanate has a tendency to pass through the filter.

The filter paper containing the sodium titanate is transferred to the beaker in which the fusion was disintegrated. Since the crucible in which the fusion was made may contain traces of sodium titanate, it is treated with hot hydrochloric acid (1:1). The solution thus obtained together with 10 cc. of concentrated hydrochloric acid is added to the beaker holding the paper. The beaker and contents are heated gently until the sodium titanate and ferric oxide, with which it is contaminated, are in solution. This solution is then filtered into a 500 cc. beaker and diluted to 300 cc. Ammonia is then added until a flocculent precipitate is formed and the solution is yet acid to litmus. One and a half cc. of concentrated hydrochloric acid are added, followed by the addition of 30 cc. of 20 per cent sodium thiosulphate solution. The solution is boiled ten minutes and the precipitated titanic acid is allowed to settle, when it is transferred to a filter, washed ten times with hot two per cent acetic acid solution, ignited, and weighed as titania, TiO_2.

COLORIMETRIC METHOD.

The filter paper containing the titanic acid, obtained as above described, is transferred to a 250 cc. beaker, together with 10 cc. of sulphuric acid (1:1). The beaker is gently heated until the titanic acid has dissolved. If necessary, additional sulphuric acid is used to insure complete solution. The titanium is determined colorimetrically by comparing this solution, or an aliquot part of it, after the addition of hydrogen peroxide, with a standard solution of titanium sulphate.

PREPARATION OF STANDARD TITANIUM SULPHATE SOLUTION.

Twenty-six hundredths of a gram of ignited titania is fused with six grams of sodium carbonate, the fusion is disintegrated in 50 cc. of water. and the crucible and lid are placed therein. After warming for an hour with 100 cc. sulphuric acid (1:4), solution will usually be complete. This solution is transferred to a 250 cc. volumetric flask and diluted to the mark with water. The purity of the titania may be found, and the solution thus standardized, by precipitating 50 cc. of the solution with sodium thiosulphate in a slightly acid solution, as described under the gravimetric method. If the above amount of titania is taken, one cubic centimeter of the solution will equal approximately one milligram of titania.

COLOR COMPARISON.

To the unknown solution or an aliquot part of it, contained in a suitable comparison tube, 5 cc. of hydrogen peroxide are added, when the whole is diluted to a definite volume and mixed. Into a similar tube are placed 5 cc. of hydrogen peroxide, and a five per cent solution of sulphuric acid is added until the volume of the mixture is slightly smaller than the unknown solution. The standard titanium sulphate solution is now added from a burette until, after thorough mixing, the color matches that of the unknown solution, when it is diluted to the same volume, again thoroughly mixed, and its color compared with the unknown solution. The determination is completed by carefully matching the colors after the addition, if necessary, of one or more drops of the standard solution. The number of cubic centimeters of the standard solution used indicates the amount of titania present.

SHORT METHOD—COLORIMETRIC.

One gram of the sample is fused with 5 grams of sodium carbonate until the material is decomposed. The crucible, containing the fusion, and its lid are placed in a 250 cc. beaker and covered with water. Heat is applied, and, when all soluble salts are in solution, the crucible and lid are removed. The solution is diluted to 200 cc., boiled a few minutes, and the insoluble part, which contains all the titanium as sodium titanate, is collected on a filter and washed with two per cent sodium carbonate solution. The paper and precipitate are returned to the 250 cc. beaker. Since the crucible in which the fusion was made may hold some adhering sodium titanate, it is treated

with 10 cc. of sulphuric acid (1:1). This acid solution is transferred to the beaker containing the paper and precipitate, and enough heat is applied to dissolve the salts, but not to char the paper. When solution has been effected, the paper is separated by filtration and washed. The titanium in the filtrate is determined colorimetrically on the whole solution, or on an aliquot part, as described in the preceding method.

LIME.

VOLUMETRIC METHODS.

METHOD USING FILTRATE FROM AMMONIUM HYDRATE SEPARATION.

The filtrate from the ammoniacal precipitation of the aluminum, iron, manganese, and titanium is diluted to about 350 cc. and heated to boiling. Then 30 cc. of a saturated solution of ammonium oxalate and 10 cc. of ammonia are added, the latter drop by drop, to precipitate the lime. After boiling ten minutes with stirring to prevent bumping of the solution, the precipitate is allowed to settle and is separated on a 11 cm. filter. If it is suspected that the magnesia content exceeds .03 gram (3.0 per cent on a one gram sample or 6.0 per cent on a half gram sample), the calcium oxalate is dissolved on the filter with hot hydrochloric acid (1:1). The solution is received in the beaker in which the precipitation was made, and the lime is reprecipitated by 5 cc. of ammonium oxalate and 5 cc. of ammonia in excess. The calcium oxalate is washed with hot water and dissolved from the filter in hot sulphuric acid (1:4), whereupon the solution is diluted to 200 cc. with boiling hot water and titrated at 80°C. with potassium permanganate solution, which has been standardized by means of sodium oxalate. The number of cubic centimeters of standard potassium permanganate solution required for the titration multiplied by the calcium oxide factor of one cubic centimeter of the permanganate solution and divided by the initial weight of the sample equals the per cent lime. Sulphuric acid that is employed in the titration of lime should be boiled before using to expel any reducing substances such as sulphur dioxide.

SOLUTION USED.

Standard Potassium Permanganate Solution.

Potassium permanganate	5.7 grams
Water	1000 cc.

The potassium salt is dissolved in boiling water, and the solution is permitted to stand for 24 hours. It is then filtered through an asbestos filter and standardized as follows: From a stoppered bottle .25 to .3 gram of standard sodium oxalate is accurately weighed and dissolved in 200 cc. of water and 10 cc. of sulphuric acid (1:1). The solution is heated to 80°C. and titrated with the permanganate solution to a faint permanent pink. The weight of sodium oxalate is multiplied by .4184, the equivalent of 1 gram of sodium oxalate in terms of calcium oxide, and the product is divided by the number of cubic centimeters of permanganate used. This figure is the value of 1 cc. of permanganate solution in terms of calcium oxide.

SHORT METHOD—LIME AND MAGNESIA.

Lime and magnesia may be determined in the presence of iron, aluminum, and manganese after the removal of the silica. The filtrate from the silica separation is heated to boiling, and the iron is oxidized by the addition of a few drops of nitric acid. The solution is cooled, and 6 to 10 grams of citric acid are added, followed by ammonia to a slight excess. The solution is heated to boiling, whereupon 30 cc. of a saturated solution of ammonium oxalate are added, drop by drop, to precipitate the lime. The determination is concluded as in the preceding method, the filtrate being used for the determination of magnesia.

SHORT METHOD—LIME ONLY.

When the determination of magnesia is not required, the lime may be determined in the presence of silica, iron, aluminum, and manganese by the use of free oxalic acid in the precipitation. One-half to one gram of the sample is suspended in 100 cc. of hot water, and 10 cc. of concentrated hydrochloric acid are added. When solution is complete, ammonium hydroxide is added until a faint precipitate forms. This is dissolved by the addition of 10 cc. of a ten per cent solution of oxalic acid. After diluting the solution to 200 cc. and boiling, 30 cc. of a saturated solution of ammonium oxalate are added, drop by drop, and the determination of lime is finished as in the preceding methods.

GRAVIMETRIC METHOD.

The filtrate from the oxide method for alumina is treated as in the first method under volumetric methods for lime, but instead of titrating the pre-

cipitate of calcium oxalate, it and the filter paper are placed in a weighed platinum crucible, ignited, cooled in a desiccator, and weighed as calcium oxide. When extreme accuracy is desired, the ignited and weighed precipitate is dissolved in warm hydrochloric acid (1:1), and the solution is evaporated to dryness. After baking, as in the determination of silica, the residue is treated with hydrochloric acid (1:1), and the silica is determined and deducted from the weight of impure calcium oxide.

MAGNESIA.

The filtrate, or filtrates, from the calcium oxalate precipitation in any method, excepting the short one for lime only, is evaporated to 200 cc. in volume and made slightly acid with concentrated hydrochloric acid, when 5 cc. of a ten per cent solution of ammonium phosphate are added. To the cold solution, concentrated ammonia is added, drop by drop and with constant stirring, until distinctly alkaline. The solution is stirred at intervals for two or three hours, or preferably agitated mechanically for about one hour. If permissible, it is then allowed to stand in a cool place over night. The solution is filtered, and the precipitate is washed with dilute ammonia (1:4). The paper and contents are placed in a weighed platinum crucible and ignited at a low temperature until the filter is destroyed and finally at the highest temperature of the Meker burner, muffle furnace, or blast lamp. The residue is magnesium pyrophosphate, and it contains 36.21 per cent of magnesia.

When extreme accuracy is desired, the precipitate of magnesium phosphate is dissolved on the filter with the least possible amount of cold hydrochloric acid (1:1). The solution thus obtained is diluted to about 100 cc., and several drops of ammonium phosphate solution are added, followed by ammonia, drop by drop, with constant stirring. When the crystalline precipitate has formed, 5 cc. of concentrated ammonia in excess are added. The solution and precipitate are agitated and allowed to stand for several hours. The precipitate is then collected on a filter and washed thoroughly with ammonia (1:4).

The filtrate from the first precipitation of magnesium phosphate should also be examined for magnesia, unless care has been taken to keep the quantity of ammonium salts, particularly ammonium chloride, at the minimum. The filtrate is evaporated to dryness in a dish, and the bulk of the ammonium salts is expelled by heating. The residue is dissolved in about 75 cc. of water, and

the solution is filtered, if necessary. A few drops of ammonium phosphate solution are added, followed by a few drops of ammonia. The solution is stirred and permitted to stand a short time. If any magnesium phosphate separates, the amount of magnesia is determined and added to the amount previously obtained.

IRON.

Five grams of the sample are sintered with an equal weight of sodium carbonate in a muffle furnace or over a strong blast for 20 to 30 minutes. The sintered mass is dissolved in 30 cc. of hot hydrochloric acid (1:1), and the solution is heated to boiling, when the iron is reduced by the addition of stannous chloride solution from a burette, drop by drop, until the brown color disappears. One drop in excess is then added. Three hundred cubic centimeters of cold water are added, followed by 5 cc. of mercuric chloride solution with constant stirring. After the addition of 10 to 30 cc. of manganese sulphate solution, the solution is titrated with thirtieth normal standard potassium permanganate.

The number of cubic centimeters of standard potassium permanganate solution required for the titration is multiplied by the value in iron of one cubic centimeter of the standard solution and 100. The product, divided by the number of grams of the material taken for analysis, gives the percentage of iron in the sample.

SOLUTIONS USED.

Thirtieth Normal Potassium Permanganate Solution.

Potassium permanganate	1.06 grams
Water	1000 cc.

This solution is prepared and standardized as described under the determination of lime in blast furnace slags. One-tenth gram of sodium oxalate, accurately weighed, is used for the standardization. The value in iron of one cubic centimeter of the standard permanganate solution is found by the following calculation:

$$\frac{.083337}{\text{(Volume in cubic centimeters of permanganate solution required to oxidize .1 gram of sodium oxalate.)}}$$

The figure .083337 is the weight of iron, expressed as the fraction of a gram, which is equivalent to .1 gram of sodium oxalate.

Stannous Chloride Solution.

Stannous chloride	250 grams
Hydrochloric acid, 1.19 sp. gr.	500 cc.
Water	500 cc.

Mercuric Chloride Solution.

Cold saturated solution.

Manganese Sulphate Solution.

Manganese sulphate	90 grams
Water	650 cc.
Sulphuric acid, 1.84 sp. gr.	175 cc.
Phosphoric acid, 1.75 sp. gr.	175 cc.

MANGANESE.

One-tenth to two-tenths gram of the sample is transferred to a 250 cc. beaker and moistened with 10 cc. of water, when 10 cc. of concentrated nitric acid are added. The contents of the beaker are boiled until the slag is decomposed. Fifteen cubic centimeters of silver nitrate solution are added, and the volume is brought to 100 cc. by dilution with water. The manganese is oxidized by adding 1 gram ammonium persulphate and heating the solution to boiling. After cooling below 20°C., the solution is titrated rapidly with standard sodium arsenite solution to the first disappearance of the pink color.

SOLUTIONS USED.

Silver Nitrate Solution.

Silver nitrate	1.333 gram
Water	1000 cc.

Standard Sodium Arsenite Solution.

Sodium arsenite	1.1 gram
Water	1000 cc.

The solution is standardized by means of a standard steel of known manganese content. It is adjusted, if necessary, so that one cubic centimeter is equivalent to one-tenth per cent manganese based on an initial weight of two-tenths gram of the sample.

SULPHUR.

VOLUMETRIC METHODS.

Direct Titration Method.

One-half gram of the sample is suspended in 50 cc. of cold water in a small beaker or flask, and 10 cc. of starch solution are added. A slight estimated deficiency of standard iodine or potassium iodate solution is added from a burette, followed by 50 cc. hydrochloric acid (1:1) and stirring. As the blue color disappears, more titrating solution is added until the blue end point is permanent. Solutions required are made as directed in the evolution method which follows.

Evolution Method.

A simple and convenient apparatus for the determination of sulphur by the evolution method may be constructed with a 300 cc. flask and suitably bent glass tubing. The flask is closed by a two hole rubber stopper equipped with a long-stemmed funnel or thistle tube and a glass exit tube bent at a right angle. The latter is connected, by means of pure rubber tubing, to a similar tube which extends to the bottom of the absorption vessel. The absorption of the evolved gases may be conducted either in a tall 500 cc. beaker, in which the subsequent titration is effected, or in a large test tube, 10″x 1″.

Two-tenths gram of the sample and a small piece of stick zinc weighing about 2 grams are transferred to the flask. The function of the stick zinc is to generate hydrogen. The stopper is inserted, and the flask is connected to the absorption vessel. Ten to twenty cubic centimeters of the absorbent solution are added to the absorption vessel and diluted to 60 or 200 cc., depending upon whether a test tube or a beaker is employed. Eighty cubic centimeters of hydrochloric acid (1:2) are added to the flask, and heat is applied so that a continuous brisk evolution of gases results until the slag and zinc metal are in solution. At this point, the heat is increased until the solution of the slag is boiling and the gases in the flask are completely displaced by the resulting steam. The flask is then disconnected from the absorption vessel.

If the absorption was effected in a beaker, 10 cc. of starch solution are added, and the delivery tube is removed and washed alternately with a jet of cold water and of hydrochloric acid (1:2) until free from traces of the

absorbent solution and adhering particles of the precipitate. If the absorption was effected in a test tube, its contents are transferred to a 500 cc. beaker, containing 10 cc. of starch solution, and the tubes are washed as detailed above. In the use of standard iodine solution, it is quite essential, before the iodine solution is added, that a slight excess of acid is present; otherwise, the alkali of the absorbent solution will combine with the iodine, which may not be completely liberated upon subsequent acidification. The solution, after acidification, is diluted to 400 cc. with cold water and is gently stirred. The standard iodine or potassium iodate solution is then admitted from a burette in successive portions with gentle stirring, until the blue color fades slowly. At this point, the titrating solution is added cautiously until the addition of a final drop yields a blue color which persists upon continued stirring. Each cubic centimeter of iodine or iodate solution added equals .0005 gram sulphur. The percentage sulphur in the sample is found by multiplying the number of cubic centimeters of the titrating solution by .0005 and 500.

Sulphur, which is present in slags as the sulphide, is calculated to calcium sulphide by multiplying by the factor 2.25 and reported as such. The calcium, thus calculated as the sulphide, is computed to calcium oxide by multiplying the percentage sulphur by the factor 1.75, and the amount found thereby is subtracted from the total lime.

SOLUTIONS USED.

Starch Indicator.

An emulsion of 6 grams of starch in 100 cc. of cold water is cautiously added to a liter of boiling water contained in a suitable flask. After continued boiling for five minutes, the flask and contents are cooled, and 6 grams of zinc chloride dissolved in 50 cc. of cold water are added to preserve the solution. After thoroughly mixing its contents, the flask is set aside for 24 hours and occasionally shaken. When the heavier particles have settled, the supernatant liquid is carefully decanted into a suitable container.

It is recommended that the starch be added to boiling water, as this tends to lessen the often unavoidable frothing; should frothing occur, however, its subsidence may be effected by playing a jet of air over the surface of the boiling solution.

If desired, the starch indicator solution may be added to any of the stock absorbent solutions in such proportions as to furnish the equivalent of 10 cc. of the indicator in the titration.

Standard Iodine Solution.

Potassium iodide	10 grams
Iodine	4.5 grams
Water	1000 cc.

The iodine and potassium iodide are transferred to a graduated one liter flask, 25 cc. of cold water are added, and the flask is shaken until the iodine has dissolved. The solution is then diluted to one liter and set aside for not less than 24 hours before standardizing. A standard steel, the sulphur content of which is between .050% and .070% and has been accurately determined, is conveniently used for standardizing the iodine solution. One cubic centimeter of this solution, after adjustment, if necessary, is equivalent to .0005 gram sulphur or to .01 per cent sulphur based upon an initial weight of five grams of the steel sample.

Standard Potassium Iodate Solution.

Potassium iodate	1.20 grams
Potassium iodide	12 grams
Potassium hydroxide	2 grams
Water	1000 cc.

The salts are dissolved in 300 cc. of water. This solution is then diluted to one liter and standardized in the same manner as the standard iodine solution.

ABSORBENTS.

Ammoniacal Cadmium Chloride Solution.

Cadmium chloride	5 grams
Water	375 cc.
Ammonia, .90 sp. gr	625 cc.

Caustic Alkali Solution.

Sodium or potassium hydroxide	5 grams
Water	1000 cc.

Ammoniacal Zinc Sulphate Solution.

Zinc sulphate	10 grams
Water	375 cc.
Ammonia, .90 sp. gr	625 cc.

GRAVIMETRIC METHODS.

METHOD FOR SULPHATE SULPHUR IN WEATHERED SLAGS.

Sulphur in the form of sulphates, in weathered or granulated slags, is determined on a one gram sample. After removing the silica, as in the determination of this constituent, the filtrate from the dehydrated silicic acid is heated to the boiling point, 5 cc. of a 10 per cent solution of barium chloride are added, drop by drop with stirring, and the container is placed on a steam bath or hot plate until the precipitate has subsided. The precipitate is then transferred to a filter, washed with hot water until free from chlorides, ignited in an open crucible, and weighed; 13.73 per cent of this weight is equivalent to sulphur, or 34.30 per cent to sulphur trioxide.

METHOD FOR TOTAL SULPHUR.

One gram of the sample is placed in a porcelain dish and covered with bromine water. Thirty cubic centimeters of concentrated nitric acid and 20 cc. of concentrated hydrochloric acid are added. Heat is applied until the sample is dissolved, whereupon the solution is evaporated to dryness. The residue is moistened with a few cubic centimeters of hydrochloric acid (1:1), which is followed by the addition of 40 cc. of water. The contents of the dish are boiled, and the undissolved portion is separated by filtration and washed. The sulphur is precipitated in the boiling hot filtrate by means of 10 cc. of a 10 per cent barium chloride solution, added drop by drop with stirring, and the determination is concluded as described in the preceding method.

The weight of barium sulphate obtained, multiplied by the factor 13.73, gives the per cent of total sulphur in the sample. The amount of sulphur, existing in the sample as sulphate, may be found by subtracting from the percentage of total sulphur, the percentage of sulphide sulphur as established by either of the volumetric methods.

ALKALIES.

Three grams of the sample are transferred to a platinum dish and dissolved in 30 cc. of concentrated hydrochloric acid. The solution is evaporated to dryness, when the residue is moderately baked. Ten cubic centimeters of concentrated hydrochloric acid and 20 cc. of water are introduced, and the contents of the dish are digested until the soluble portion is dissolved.

The residue, which is mainly silica, is separated by filtration, the filtrate and washings being received in a platinum dish. The residue is ignited in a platinum crucible and moistened with 20 drops of sulphuric acid (1:1) and about 3 cc. of hydrofluoric acid. The crucible is heated carefully until the sulphuric anhydride is expelled, whereupon the residue is dissolved in water with the aid of a little hydrochloric acid, if necessary.

The filtrate in the platinum dish is made ammoniacal and evaporated to dryness. The residue is treated with dilute ammonia (1:4), and the contents of the dish are boiled and filtered. The residue is washed with dilute ammonia (1:4), the filtrate and washings passing into another platinum dish.

The hydrochloric acid solution of the residue, obtained on volatilization of the insoluble portion, is added to the solution just mentioned, and the combined solutions are treated as follows: Five cubic centimeters of a 10 per cent solution of barium chloride are added to the slightly acid solution to precipitate the sulphur present. The solution is filtered from the barium sulphate, and the filtrate is retained in a platinum dish. To the boiling filtrate, 5 cc. of a 20 per cent solution of ammonium carbonate containing 20 per cent of concentrated ammonium hydroxide are added. The solution is boiled a few minutes and filtered into another platinum dish, when the filtrate is evaporated to dryness. The dish and residue are carefully heated to expel ammonium salts, a few cubic centimeters of hot water are added, and the small amount of lime remaining is separated with a few drops of ammonium oxalate solution and ammonium hydroxide. The resulting filtrate, received in an untared platinum crucible of 30 to 35 cc. capacity, is evaporated to dryness, and the crucible is gently ignited. The residue is moistened with hydrochloric acid, the solution is evaporated to dryness, and the crucible and contents are ignited at a dull red heat to constant weight. Care must be exercised in this ignition that the temperature does not reach a point sufficiently high to cause the loss of the alkali chlorides by volatilization. The contents of the crucible are digested in hot water, the solution is filtered, the filtrate being recovered in a small porcelain dish, and the filter, containing the slight insoluble residue, is returned to the original crucible, which is again ignited and weighed. The difference in weight represents the combined weight of sodium and potassium chlorides. The separation of the alkalies is then made either by the direct or the indirect method.

Notwithstanding care in manipulation and the use of the purest reagents obtainable, a positive result will always be found in a blank test. This test should be made under the same conditions as described in the regular method, and the result so obtained is deducted from the combined weight of the chlorides in the regular determination.

DIRECT METHOD.

To the solution of the chlorides in the porcelain dish, an excess of platinic chloride solution is added, and evaporation is conducted on a water bath in an atmosphere free of ammonia, until the liquid solidifies on cooling. It is then drenched with 80% alcohol, which is poured upon a small filter, and the residue is washed by decantation with alcohol of the same strength. Both dish and filter are freed from any residual alcohol by careful heating; the dish is cleansed with a minimum of hot water, the water solution being transferred through the filter into a weighed crucible. The crucible, which contains all the potassium platinic chloride in solution, is heated in an air bath to expel the water. The temperature is gradually increased to a maximum of 135° C., which is maintained for fifteen minutes.

The crucible is then cooled and weighed, and the increase in weight, representing potassium platinic chloride, minus the weight found in the blank, is multiplied by .1938, which yields the equivalent of potassium oxide. The weight of potassium oxide, multiplied by 1.5830, is equivalent to grams potassium chloride, which, deducted from the combined weight of the chlorides as previously ascertained, yields the weight of sodium chloride. The weight of sodium chloride, multiplied by .5303, is equivalent to grams of sodium oxide. The several equivalents thus obtained are corrected to their respective percentage values.

INDIRECT METHOD.

To the solution of the chlorides of sodium and potassium in a porcelain dish, one cubic centimeter of a one per cent solution of potassium chromate is added as an indicator, and the chlorine is titrated with silver nitrate solution. A titration is also made in the same manner with the solution of the chlorides obtained in the blank and the result deducted. The silver nitrate solution contains 4.791 grams silver nitrate crystals per liter, and 1 cc. is equivalent to 1 mg. chlorine. From these two results—the total chlorides and chlorine—

the oxides of the alkalies may be calculated by the following formulae, the derivation of which is shown below.

$$K_2O = 2.925 \text{ x chlorides} - 4.822 \text{ x chlorine.}$$

$$Na_2O = 4.048 \text{ x chlorine} - 1.925 \text{ x chlorides.}$$

Total alkali oxides = (chlorides — .774 x chlorine).

Derivation of formulae for calculation of alkali oxides from the total chlorides and chlorine.

Let x = Na_2O,

y = K_2O,

a = total chlorides,

and b = total chlorine.

$$31 : 58.46 :: x : \frac{58.46}{31} x.$$

($\frac{1}{2}$ Na_2O : NaCl)

$$\text{Hence, } \frac{58.46\ x}{31} = NaCl.$$

$$47.1 : 74.56 :: y : \frac{74.56}{47.1} y.$$

($\frac{1}{2}$ K_2O : KCl)

$$\text{Hence, } \frac{74.56\ y}{47.1} = KCl.$$

$$(1) \quad \frac{58.46\ x}{31} + \frac{74.56\ y}{47.1} = a.$$

$$31 : 35.46 :: x : \frac{35.46}{31} x.$$

($\frac{1}{2}Na_2O$: Cl)

$$\text{Hence, } \frac{35.46\ x}{31} = \text{Chlorine combined with sodium.}$$

$$47.1 : 35.46 :: y : \frac{35.46}{47.1} y.$$

$$\text{Hence, } \frac{35.46\ y}{47.1} = \text{Chlorine combined with potassium.}$$

$$(2) \quad \frac{35.46\ x}{31} + \frac{35.46\ y}{47.1} = b.$$

From (1) and (2), the following equations are derived:

$$y = 2.925\ a - 4.822\ b.$$

$$x = 4.048\ b - 1.925\ a.$$

$$x + y = a - .774\ b.$$

Error of determining alkalies by the indirect method.

The statement is often made that this method is accurate only when both alkalies are present to considerable extent. From the formula for potassium oxide, (2.925 x chlorides — 4.822 x chlorine), it is readily seen that an error in determining the chlorides and the chlorine is magnified three and five times, respectively. Likewise in calculating the sodium oxide, the error is magnified two and four times, respectively. In general then, an error of determination is multiplied in the calculation by a number less than five.

ANALYSIS OF MISCELLANEOUS SLAGS, CINDERS, AND SCALES.

(SUCH AS OPEN HEARTH AND CONVERTER SLAGS, HEATING FURNACE CINDER, AND ROLL SCALE.)

SILICA.

The sample is finely ground in an agate mortar, and 1 to 2.5 grams, according to the amount of silica suspected, are taken for analysis. In the analysis of materials containing a high percentage of lime, the method for the determination of silica is the same as for blast furnace slags. For other materials, the sample is digested in an evaporating dish with 10 to 30 cc. of concentrated hydrochloric acid. Any insoluble residue is removed by filtration, and it and the filter are ignited until the paper is destroyed, when the residue is fused with 2 to 3 grams of sodium carbonate. The fusion is added to the soluble portion, and the silicic acids are dehydrated as described under blast furnace slags. In case of material very insoluble in hydrochloric acid, the entire sample is fused in a large platinum crucible with five times its weight of sodium carbonate. The fusion is leached in hot water, and the solution is kept just below the boiling temperature until the melt is disintegrated, whereupon it is acidified with hydrochloric acid and evaporated to dryness. The determination is concluded as for silica in blast furnace slags.

If analysis for other constituents is desired, the filtrate from the silica is received in a volumetric flask, and aliquot portions of this solution are taken for these determinations, where possible, instead of weighing portions of the original sample for each constituent.

ALUMINA-TITANIA.

An aliquot part of the filtrate from the silica determination, representing .5 gram of the sample, is transferred to a beaker of 600 cc. capacity, and 10 cc. of concentrated hydrochloric or nitric acid are added. Two basic acetate separations of aluminum, iron, and titanium are then made as follows:

The solution is first brought to a volume of approximately 150 cc. by dilution or concentration as the case may be. The greater part of the free acid is neutralized, first with concentrated ammonia, then cautiously with dilute ammonia (1:4) or ammonium carbonate, with vigorous stirring, until a faint precipitate persists. The solution is then diluted with hot water to about 400 cc., when 25 cc. of a 20 per cent solution of ammonium acetate

are added. The solution is heated to the boiling point and allowed to boil one minute. After the precipitate has subsided, the solution is filtered through an 18.5 cm. filter on a 4 inch ribbed funnel, and the filtrate is retained in an 800 cc. beaker. The precipitate is washed once with hot water. It is then dissolved in hot hydrochloric acid (1:1), and the basic acetate separation is made in the resultant solution as before, except the dilution before precipitation need not be so great. The residue on the filter is dissolved in hydrochloric acid (1:1), and the solution is used for the determination of alumina.

In routine work or in case extreme accuracy is not required, the second precipitation by ammonium acetate may be omitted.

The combined filtrates and washings are concentrated to a volume under 200 cc., and if any alumina separates, it is removed by filtration, washed, and dissolved in hydrochloric acid (1:1), the solution being combined with the solution of the basic acetate precipitate. The concentrated filtrate, now freed from all traces of alumina, is reserved for the separation of manganese.

METHOD FOR ALUMINA DETERMINATION—TITANIUM ABSENT.

The combined hydrochloric acid solutions of the basic acetate precipitate and traces of recovered alumina, if any, are diluted to 400 cc. in a 600 cc. beaker. To the cold solution, 30 cc. of a 10 per cent solution of ammonium phosphate are added. A few drops of methyl orange or litmus solution are then added as an indicator, followed by ammonia until the solution is just neutral. One and one-half cubic centimeters of concentrated hydrochloric acid are then added, the solution is stirred until clear, and 50 cc. of a 20 per cent solution of sodium thiosulphate are added. The solution is heated just to the boiling point, 8 cc. of glacial acetic acid and 15 cc. of a 20 per cent solution of ammonium acetate are added, and the boiling is continued for ten minutes. The precipitate of aluminum phosphate is allowed a few minutes to subside, when it is collected as quickly as possible on a filter and washed twice with hot water. The precipitate contains an appreciable amount of iron, which is removed by making a second precipitation. The impure aluminum phosphate is dissolved in hot hydrochloric acid (1:1); the solution is received in the beaker in which the first precipitation was made and diluted to 300 cc., whereupon the precipitation is made as before. When speed is paramount, the second precipitation may be eliminated at the discretion of the operator. The precipitate is washed ten times with hot

water and ignited at a low temperature in a porcelain crucible until the carbon is destroyed, then at the highest temperature of the Meker burner or muffle furnace. When cool, it is weighed as aluminum phosphate, 41.84 per cent of which is alumina.

METHOD FOR ALUMINA DETERMINATION—TITANIUM PRESENT.

The combined hydrochloric acid solutions of the basic acetate precipitate and traces of recovered alumina, if any, are used.

To the cold solution, diluted to 300 cc., concentrated ammonia is added, drop by drop, until a slight permanent precipitate is formed. One and one-half cubic centimeters of concentrated hydrochloric acid are added, and, after the precipitate has dissolved, 50 cc. of a 20 per cent solution of sodium thiosulphate and 10 cc. of acetic acid, in the order named, are added. The solution is boiled ten minutes; the titanic acid is thus completely precipitated, but is accompanied, however, by a part of the alumina and phosphoric acid and a small amount of iron. After allowing a few minutes for the precipitate to settle, the solution is filtered, the filtrate being received in an 800 cc. beaker, and the precipitate is washed with a hot two per cent solution of acetic acid.

To the filtrate, 30 cc. of a ten per cent solution of ammonium phosphate and one and one-half cubic centimeters of concentrated hydrochloric acid are added. If a precipitate remains after stirring thoroughly, another portion of concentrated hydrochloric acid is added, and the solution is stirred until the precipitate dissolves. Thirty cubic centimeters of sodium thiosulphate solution are now added. The solution is heated to boiling, 15 cc. of a twenty per cent solution of ammonium acetate are added, and the boiling is continued for ten minutes. The precipitate of aluminum phosphate is allowed to settle, collected on a filter, and washed with hot water. It is dissolved on the paper with very hot hydrochloric acid (1:1), the solution being received in the beaker in which the precipitation was effected. This solution is reserved for a second precipitation of alumina after the alumina which is recovered from the preliminary titanic acid precipitate has been added to it. This alumina is recovered as follows:

The impure titanic acid precipitate is ignited in a platinum crucible, and the contents of the crucible, which consist of all the titania, a small quantity of the alumina, part of the phosphorus, and some iron, are fused with sodium carbonate. The fusion is disintegrated in 50 cc. of hot water in a beaker of 250 cc. capacity, when the contents of the beaker are

heated to a boiling temperature for ten minutes. The insoluble matter is allowed to settle, and the solution is filtered through a close filter from the sodium titanate and ferric oxide. The filtrate is retained in a 400 cc. beaker, and the residue is washed with a one per cent solution of sodium carbonate. It may be necessary to refilter the solution, as the sodium titanate has a tendency to pass through the filter. The residue on the filter is reserved for the determination of titania, if desired.

The clear filtrate is added to the solution of the aluminum phosphate precipitate. The alumina is now reprecitated as aluminum phosphate, and the determination is finished by the preceding method for alumina in the absence of titanium.

TITANIA.

The filter paper, containing the sodium titanate obtained in the determination of alumina in presence of titanium, is transferred to the 250 cc. beaker in which the fusion was disintegrated. The residue in the fusion crucible and the main precipitate in the beaker are dissolved in hydrochloric acid, and the determination is finished either gravimetrically or colorimetrically as described under titania in blast furnace slags.

MANGANESE.

METHOD USING FILTRATE FROM ACETATE SEPARATION.

The filtrate obtained upon removing the traces of alumina after the basic acetate precipitation, at a volume of 200 cc., is heated, and, while boiling, a solution of one gram of ammonium persulphate and 25 cc. of ammonia, in the order named, are cautiously added. The solution is then stirred vigorously. After boiling for about ten minutes, the precipitate is collected on a filter paper and washed with hot water. The filtrate is retained in a 400 cc. beaker for the determination of lime and magnesia.

The manganese dioxide is dissolved on the paper with hot hydrochloric acid (1:1). A little sulphurous acid may be used to aid in dissolving this precipitate. The solution is received in the beaker in which the precipitation was made, thereby recovering any manganese precipitate which may have adhered to the sides of the beaker. The solution is boiled to expel the excess sulphurous acid, whereupon the determination is finished at the option of the operator by either the chlorate-oxalate or the persulphate-arsenite method.

CHLORATE-OXALATE METHOD.

Fifty cubic centimeters of concentrated nitric acid are added to the solution of manganese in the beaker. The liquid is rapidly evaporated, with a cover on the beaker, to a volume of 10-15 cc. The evaporation is repeated with 50 cc. additional nitric acid to remove all hydrochloric acid. Seventy-five cubic centimeters of concentrated nitric acid are introduced, and, after boiling for five to ten minutes to expel nitrous fumes, the beaker is removed from the light and cooled to room temperature. Four grams of sodium or potassium chlorate are cautiously added, the solution is heated to boiling, and the boiling is continued for ten minutes. The addition of the chlorate to the cold solution greatly facilitates the subsequent decomposition of the manganese dioxide in the sodium oxalate-sulphuric acid solution. The beaker and contents are removed from the heat. and the precipitate of the manganese dioxide is separated by filtration through an asbestos plug. The latter is contained in a carbon filter tube and has been previously washed with nitric acid. The precipitate is washed twice with concentrated nitric acid which is free from nitrous fumes. This is prepared by bubbling air through concentrated nitric acid for thirty minutes. The beaker and precipitate are washed with cold water. The plug and precipitate are transferred to the original beaker. and adhering traces of manganese dioxide are washed from the carbon filter tube with boiling water. Sufficient boiling hot water is then added to make a volume of about 100 cc. Twenty-five cc. of sulphuric acid (1:1) are added, followed by .2 gram of sodium oxalate, accurately weighed. A weight of .2 gram of sodium oxalate is sufficient to use for .5 gram of a sample which has a manganese content of 8 per cent or less. In case of a larger initial weight of the sample or a sample of material containing a greater per cent of manganese, a corresponding increase is made in the amount of sodium oxalate used. The contents of the beaker are shaken or stirred until the precipitate is completely dissolved. Should pieces of the precipitate dissolve with difficulty, these are crushed with a stirring rod until no more particles of manganese dioxide may be seen on looking through the bottom of the beaker. When the precipitate has completely dissolved, the solution is heated to 65°C., and the excess of sodium oxalate is rapidly titrated with a twentieth normal solution of potassium permanganate. The end point is the first pink tint which persists for

thirty seconds. The manganese dioxide obtained from one-half gram of a sample containing 8 per cent of manganese requires for its reduction about one-tenth gram of the sodium oxalate added, which leaves an excess of sodium oxalate amounting to approximately one-tenth gram.

The amount in cubic centimeters of standard permanganate solution equivalent to .2 gram of sodium oxalate minus the number of cubic centimeters of permanganate solution used in the titration, multiplied by the manganese factor of one cubic centimeter of standard potassium permanganate solution and 200, equals the percentage of manganese in the sample.

Example.

25 cc. potassium permanganate solution equals .1 gram sodium oxalate.

Volume potassium permanganate solution to titrate sample equals 26 cc.

Then, 50 cc. potassium permanganate solution are equivalent to .2 gram sodium oxalate, and (50 — 26) x manganese factor x 200 equals the percentage of manganese in the sample.

SOLUTION USED.

Twentieth Normal Potassium Permanganate Solution.

Potassium permanganate.....1.58 grams

Water.....1000 cc.

The salt is dissolved in boiling water, and the solution is permitted to stand for 24 hours. It is then filtered through an asbestos filter and standardized by titrating one-tenth gram of sodium oxalate, accurately weighed and dissolved in hot water and sulphuric acid (1:1), as described in the regular analysis. The manganese value of one cubic centimeter of the standard permanganate solution is found by the following calculation:

$$\frac{.0409895}{\text{(Volume of permanganate solution required to oxidize .1 gram of pure sodium oxalate.)}}$$

The figure .0409895 is the manganese equivalent, expressed in the fraction of a gram, of .1 gram of sodium oxalate.

PERSULPHATE-ARSENITE METHOD.

The solution of manganese, after the elimination of the excess sulphurous acid, is cooled, transferred to a volumetric flask, and diluted to the mark. An aliquot part, containing about one milligram of manganese, is pipetted

into a small beaker, 10 cc. of sulphuric acid (1:1) are added, and the solution is evaporated until fumes of sulphuric anhydride appear. The beaker and contents are allowed to cool, when 10 cc. of water are cautiously added, followed by 15 cc. of a solution of silver nitrate. The subsequent operations are the same as in the method for manganese in blast furnace slags.

The percentage of manganese in the sample is found by multiplying the number of cubic centimeters of standard arsenite solution used in the titration by the percentage manganese factor of the solution and dividing the product by a figure which is the fractional part of one gram represented by the aliquot portion measured for analysis.

Example.

Number of cubic centimeters of arsenite solution required in titration..... 4.1

Percentage manganese factor of one cubic centimeter of arsenite solution based on one gram of sample..... .02

Fraction which is equivalent to aliquot of solution used.....1/50

Then, $\frac{4.1 \times .02}{1/50} = 4.10$ per cent.

METHOD USING FILTRATE FROM DETERMINATION OF SILICA.

Manganese may be determined directly in the filtrate from the determination of silica by either of the above methods. The filtrate, or an aliquot part, is evaporated to a volume of 50 cc. when it is ready for the repeated evaporations with nitric acid and further operations as explained in the chlorate-oxalate method. If the persulphate-arsenite method is used, an aliquot portion, containing about one milligram of manganese, of the filtrate from the silica is evaporated with sulphuric acid in a small beaker to expel the hydrochloric acid, whereupon the determination is concluded as in the preceding method.

DIRECT METHOD.

One-tenth gram of the sample is placed in a small beaker and dissolved in 50 cc. of nitric acid (sp. gr. 1.20). The solution is transferred to a volumetric flask. An aliquot part, containing approximately one milligram of manganese, is measured into a beaker, 15 cc. of silver nitrate solution are added, and the analysis is concluded as in the persulphate-arsenite method previously described.

LIME AND MAGNESIA.

The analysis for these constituents is conducted on the filtrate from the manganese separation by the same methods as used for blast furnace slags. When the lime content is under five per cent, the gravimetric method is preferable, but for larger amounts, the volumetric method is recommended.

If the solution in which the lime is to be determined is colored by the presence of chromium salts, it is acidified with hydrochloric acid. The chromium is reduced by addition of a few drops of sulphurous acid, whereupon ammonia is added in excess and the solution is evaporated until the chromium is precipitated as chronium hydroxide. This precipitate is removed by filtration, and lime is determined in the filtrate.

Frequently in the determination of magnesia, in particular when two basic acetate separations have been made, the quantity of ammonium salts in the solution is so large that it interferes with the precipitation. In this case, it will be necessary, after the lime has been separated, to evaporate the solution to dryness and to expel the excess of ammonium salts by volatilization. The residue is dissolved in hydrochloric acid (1:1) and water, and the magnesia is precipitated as designated above.

IRON.

TOTAL COMBINED IRON.

METHOD USING FILTRATE FROM DETERMINATION OF SILICA.

An aliquot part (equivalent to .5 to 1 gram of the sample, depending on the iron content) of the solution from the silica determination is measured into a 400 cc. beaker. Five cubic centimeters of nitric acid are added, and the solution is heated to the boiling point. The iron is precipitated with ammonia, a liberal excess being employed, removed by filtration, washed, and dissolved in hot hydrochloric acid (1:1), the solution being received in a 400 cc. beaker.

To the hot solution, stannous chloride solution is added, dropwise, until the color due to the ferric chloride disappears. One drop is then added in excess. The solution is diluted to about 350 cc. with cold water, 5 cc. of mercuric chloride solution are added, and the contents of the beaker are thoroughly stirred. Titration of the iron with a standard potassium bichromate solution is conducted as follows:

Standard bichromate solution, almost sufficient to oxidize the iron, is added to the beaker from a burette; a test drop is transferred to a test plate; a drop of potassium ferricyanide indicator is added, and the addition of the titrating solution is continued with frequent tests until the blue tint of the ferrous iron has given away in the test drop to the yellow or brown of the oxidized iron. The iron equivalent of the amount of solution used is divided by the initial weight of the sample measured for analysis to obtain the percentage of iron.

SOLUTIONS USED.

Standard Potassium Bichromate Solution.

Potassium bichromate..... 8.9 grams
Water.....1000 cc.

The solution is standardized by means of the Corporation Iron Ore Standard, as described in Methods for the Commercial Sampling and Analysis of Iron Ores by the Chemists of the United States Steel Corporation.

Potassium Ferricyanide Indicator Solution.

Potassium ferricyanide..... 1 gram
Water.....1000 cc.

This solution is prepared daily as needed.

Stannous Chloride and Mercuric Chloride Solutions.

These are prepared in the same manner as directed for the determination of iron in blast furnace slags.

DIRECT METHOD.

One-half to one gram of the sample is transferred to a 250 cc. beaker and digested with 20 cc. of concentrated hydrochloric acid for thirty minutes. The contents of the beaker are poured upon a filter, and the residue is washed with water. The paper and residue are ignited in a platinum crucible until the paper is destroyed, whereupon the residue is fused with sodium carbonate. The fusion is leached with water, and the leachings are added to the acid soluble portion. After diluting the solution to 300 cc., 5 cc. of nitric acid are added. The temperature is raised to the boiling point, when the iron is precipitated by the addition of ammonia. The precipitate is collected on a filter paper, washed, and dissolved in hydrochloric acid (1:1). The iron in the resultant solution is titrated as explained in the preceding method.

COMBINED FERROUS IRON.

A determination of ferrous iron may be made if the sample is free from sulphides and metallic iron. One gram or more of the material, depending upon the ferrous iron content, is introduced into a suitable flask of about 300 cc. capacity, followed by approximately one gram of sodium carbonate. Twenty cubic centimeters of concentrated hydrochloric acid are poured into the flask, when it is quickly closed with a rubber stopper equipped with a Bunsen valve. After digesting over a source of heat for some time, the flask and contents are cooled; the solution is transferred to a beaker, and the ferrous iron is titrated immediately with standard potassium bichromate solution as explained in the preceding method.

METHOD FOR THE DETERMINATION OF IRON IN THE MAGNETIC PORTION.

A determination of iron in the magnetic portion of converter slags is occasionally required. This portion consists of steel shot and magnetic iron oxide. Since the steel cannot be pulverized or otherwise reduced to fineness, it is necessary to employ the mixture of shot and oxide in the original form for the analytical sample. This requires, in cases of considerable variation in the sizes of the particles of shot and oxide, some judgment on the part of the operator as to the amount of each substance which is taken for the determination in order to approximate as nearly as possible the proportion in the sample. The determination is conducted as follows:

Ten grams of the material are dissolved in 40 cc. of concentrated hydrochloric acid. The solution is transferred to a 1000 cc. volumetric flask and diluted to the mark. Fifty cubic centimeters of the solution, equivalent to five-tenths gram of the sample, are heated to boiling in a beaker, and the ferric iron is reduced with stannous chloride solution, when the determination is finished as described in preceding methods.

METHOD OF REPORTING IRON.

In reporting iron in the materials included in this chapter, the magnetic material removed in the preparation of the sample is reported as such, and the iron found in the chemical analysis is reported as combined iron and also as the proper oxide or oxides. In addition, the iron in the magnetic material is determined, or estimated, and added to the percentage of combined iron, and the sum reported as total iron.

PHOSPHORUS.

An aliquot part, representing .5 gram of the sample, of the filtrate from the determination of the silica is measured into a flask of 300 cc. capacity, or a .5 gram portion of the original sample is dissolved in concentrated hydrochloric acid or aqua regia, and the silica is removed by the usual operations, the filtrate being received in a 300 cc. flask.

The solution in either case is evaporated to a syrupy consistency, when in succession 10 cc. of concentrated nitric acid and 50 cc. of water are added. The contents of the flask are heated to boiling, 50 to 75 cc. of ammonium molybdate solution are added, and, after shaking for five minutes or standing in a warm place for thirty minutes or more, the yellow precipitate is collected on a filter and washed with two per cent nitric acid and then with water. The filter and its contents are transferred to a small flask or beaker, and an excess of the standard sodium hydroxide solution over the amount required to decompose the yellow precipitate is added. When the filter paper has been disintegrated by shaking or stirring and the precipitate has been completely dissolved, about 100 cc. of water, free from carbon dioxide, and a few drops of phenolphthalein indicator solution are introduced. The excess of sodium hydroxide solution is then titrated with standard nitric acid to the disappearance of the pink color, and the soda solution is finally added until a faint permanent pink end point is obtained. The difference between the total volumes of standard sodium hydroxide solution and of standard acid represents the phosphorus.

If preferred, the precipitate of ammonium phospho-molybdate may be weighed. In this case, the yellow precipitate is transferred to a tared paper, which has been previously dried for one hour at 110°C. and weighed between watch glasses. After washing with 2% nitric acid, the paper and contents are lightly and carefully pressed between blotting paper, dried for one hour at 110°C., and weighed between watch glasses. 1.65% of the weight of the yellow precipitate is phosphorus.

SOLUTIONS USED.

Standard Sodium Hydroxide Solution.

Sodium hydroxide..... 6.6 grams
Water.....1000 cc.

The quantity of sodium hydroxide is dissolved in 900 cc. of water. One cubic centimeter of a saturated solution of barium hydrate is added to pre-

cipitate traces of carbon dioxide. The solution is then filtered and diluted to a volume of one liter with water which is free from carbon dioxide.

Standard Nitric Acid.

Concentrated nitric acid	10 cc
Water	990 cc.

The standard acid and soda solutions are adjusted so that they exactly agree and 1 cc. is equivalent to .01 per cent phosphorus on a 2 gram sample or .04 per cent on a .5 gram sample. To confirm the solutions, they are employed in the determination of phosphorus in a steel of known phosphorus content.

Ammonium Molybdate Solution.

Molybdic acid, 85%	65 grams
Water	142 cc.
Ammonia, .90 sp. gr	143 cc.
Nitric acid, 1.20 sp. gr	715 cc.

The molybdic acid is added to the water which is held in a suitable container. The ammonia is then added with rotation of the flask until the molybdic acid is dissolved. The solution is cooled and added gradually, with constant stirring, to the nitric acid. This is allowed to stand for 12 hours before filtration, which is conducted preferably by suction through an asbestos plug.

Phenolphthalein Indicator Solution.

Phenolphthalein	1 gram
Ethyl or methyl alcohol	1000 cc.

SULPHUR.

METHODS FOR TOTAL SULPHUR.

By Solution of the Sample in Aqua Regia.

One gram of the sample is dissolved in 40 cc. of aqua regia (75% concentrated hydrochloric acid and 25% concentrated nitric acid), and the sulphur is determined gravimetrically as described in the method for total sulphur under blast furnace slags.

By Fusion with Sodium Carbonate.

One gram of the sample is fused with ten parts of sodium carbonate and one part of sodium nitrate. The fusion is dissolved in water and hydro-

chloric acid (1:1), and the solution is evaporated to dryness. The silica is separated in the usual manner, whereupon the sulphur is precipitated in the filtrate with barium chloride solution and the determination is finished as described under sulphur in blast furnace slags.

METHOD FOR SULPHIDE SULPHUR.

Sulphur, which exists in the form of sulphide, is evolved with hydrochloric acid (1:1) in the same manner as the determination of sulphur by evolution in blast furnace slags. Five grams of the sample are used, and zinc metal is employed in the operation. One cubic centimeter of the standard iodate or iodine solution is equivalent to .01 per cent sulphur when an initial weight of 5 grams of the sample is taken.

DETERMINATION OF CALCIUM CARBIDE IN ELECTRIC FURNACE SLAGS.

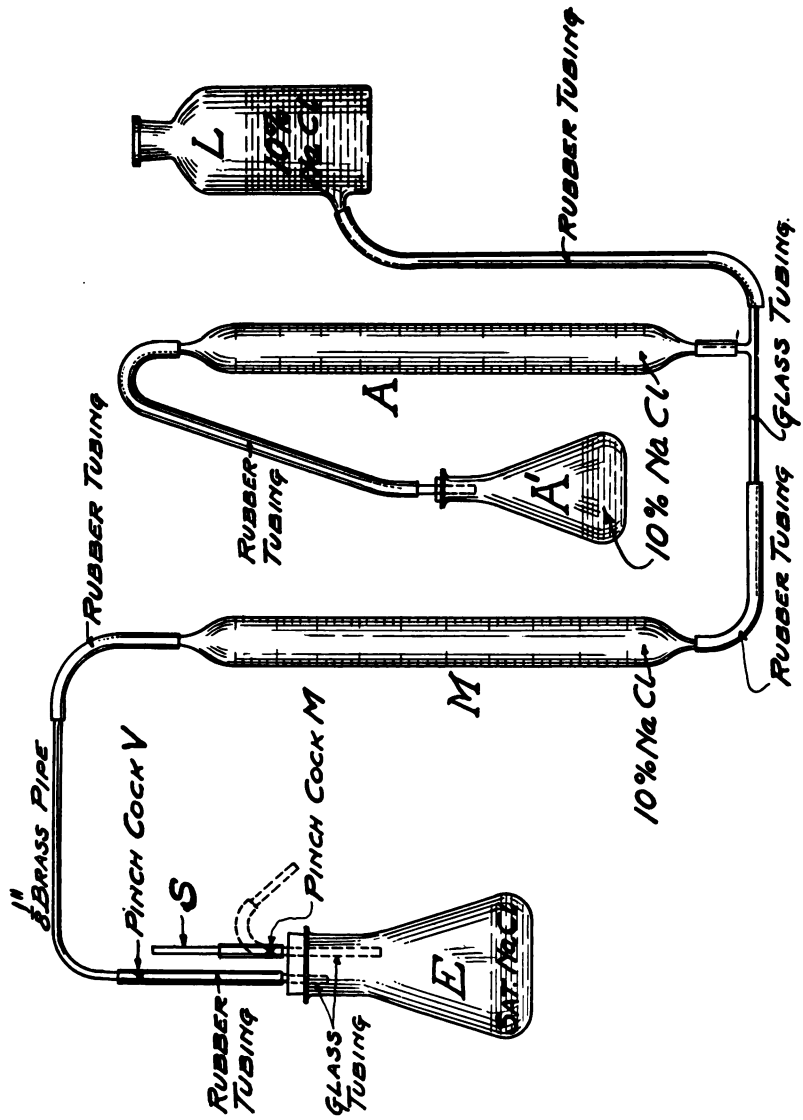
METHOD OF W. D. BROWN.

Calcium carbide in electric furnace slags is determined by slaking a sample of the slag and measuring the acetylene gas evolved. To secure measurements always under constant conditions by comparison with a gas of known volume at some standard temperature and pressure, use is made of the apparatus shown in the accompanying cut and described in the following paragraphs. The apparatus consists of the following parts:

1. Gas burette A and flask A′, connected by rubber tubing and holding about 350 cc. of air under the adopted standard condition to be later considered.

2. The measuring burette M and the generator flask E, connected by rubber tubing and a ⅛ inch brass pipe as shown. The flask E is provided with a two-hole rubber stopper. Through one hole is inserted a small glass tube by which a connection is made with the measuring burette, and through the other is inserted another glass tube, one-fourth inch in diameter, over which a one-fourth inch rubber tube is fitted. To the free end of this rubber tube, a vial S, made from a piece of glass tubing, ¼″x 3″, and containing the sample, is attached.

3. The leveling bottle L, containing a 10 per cent solution of sodium chloride. It is connected by rubber tubing and a glass T-tube with the bottom of the standard gas burette A and the measuring burette M.



APPARATUS FOR THE DETERMINATION OF CALCIUM CARBIDE IN ELECTRIC FURNACE SLAGS.

4. Upright stands to which the burettes and leveling bottle are clamped so that they can be conveniently raised or lowered. The ⅛″ brass pipe is securely held in place with a suitable clamp. The clamps and stands are not shown in the cut. The flask E is shaken on a Camp Shaking Machine, also not shown.

A standard volume of air is adopted and calculated for burette A and flask A′, and the leveling bottle L is raised or lowered so that this volume is always obtained. The water level in the measuring burette is, before each reading, brought even with the water level in A by raising or lowering burette M. By this means, the pressure in M is always the same as in A or it has the same volume as if it were under the standard conditions.

Calcium carbide reacts with water thus: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. One cubic centimeter of acetylene (C_2H_2) at 62° F. and 30″ mercury pressure weighs .0011 gram and, by the above reaction, is derived from .0027 gram CaC_2. For convenience in weighing, it is desired that 1 cc. equal .0025 gram CaC_2 so that if 2.5 grams were weighed 1 cc. would equal .1% CaC_2. Therefore, the standard gas must be lighter in the proportion of .0025 to .0027, or .926, and the gas must be expanded from 62° and 30″ so that the conversion factor would be .926, or so that the quantity

$$\frac{521}{T} \times \frac{P}{30} = .926$$

in which T is t° F.+ 459 and P is total pressure.

From the above, P = .05332 T.

If B is the barometric pressure; e, the vapor pressure at t° F.; and p, the pressure to be applied to the standard gas; then, P = B + p — e, from which p = P + e — B.

By substituting, p = .05332 T + e — B. The numerical value of p can be found by making the proper substitutions. For example, suppose that

B = 29.57″ mercury, and t = 80° F.

Then, T = 539, and e = 1.02″ mercury (From table).

Therefore, p = .05332 x 539 + 1.02 — 29.57 = .19″ mercury.

One inch of 10 per cent sodium chloride solution = .076″ mercury.

Then, .19″ mercury = 2.5″ of 10 per cent sodium chloride solution.

Therefore, the leveling bottle L must be raised so that its water level is 2.5 inches above the water level in the standing burette A. The reading of the burrette in this case is 50.0 cc. Then, before each reading is taken,

the leveling bottle must be raised or lowered so that 50 cc. is obtained on the burette. If, by any chance, the volume of air in the flask A′ is changed, this calculation must be repeated. If the value of p is found to be minus, the leveling bottle must be brought lower than the water level in the leveling burette.

Before a determination is started, the apparatus is tested. To do this, 40 to 50 cc. of a saturated solution of sodium chloride are placed in the flask E, the mouth of the flask is carefully dried, and the stopper inserted firmly by a revolving motion. The glass vial S being in place and the pinchcock V open, the leveling bottle L is raised or lowered so that the predetermined level in A is obtained. The burette M is raised or lowered so that the solution is level with that in A. A reading is taken, and E is shaken for ten minutes or more. The level of the solution in A is brought back, if necessary, and the level in M is made to agree with it. A reading is taken. It should agree with the previous reading. If it does not agree the shaking is continued, and readings are again taken until a constant volume is obtained. Any difference in the readings may be due to a leak caused by a defective connection or an ill-fitting stopper. It is well to keep the valve pinchcock M closed when the sample vial S is removed.

For the determination, 2.5 grams of the slag are weighed and transferred to the glass vial S. This vial is connected to E by the ¼″ rubber tubing which is bent over in such a manner that none of the slag enters the flask E. The vial is kept in this position by a rubber band. The pinchcock V is then opened, and the leveling bottle is raised or lowered so that the predetermined level in A is reached (in this case the 50 cc. mark). The burette M is then raised or lowered until the surfaces of the solutions in the two burettes are at the same level. A reading is taken. The vial containing the sample is inverted so that the slag falls into the flask E containing 40 to 50 cc. of saturated solution of sodium chloride. The flask is shaken for ten minutes. The leveling bottle is adjusted, if necessary, and the surface of the solution in M is brought level with that in A. A reading is again taken. The flask is again shaken for five minutes and any further evolution of gas noted. The difference between the two readings plus a blank of 1 cc. (the difference in volume between the slag in the sample vial and in the salt solution) represents the calcium carbide, 1 cc. of the increase in volume being equal to .1%.

The solution in the generator flask E need not be changed for 10 to 20 determinations.

Example.

61.3 cc.	First reading.
21.6	Second reading.
39.7	
1.0	Blank.
40.7	Volume of C_2H_2 evolved.

Therefore, the sample contains 4.07% calcium carbide.

Table 1.

Vapor pressure e at t degrees F.

t°	e	t°	e	t°	e
60	.517	70	.732	80	1.022
61	.536	71	.757	81	1.056
62	.555	72	.783	82	1.091
63	.575	73	.810	83	1.127
64	.595	74	.838	84	1.163
65	.616	75	.866	85	1.201
66	.638	76	.896	86	1.241
67	.661	77	.926	87	1.281
68	.684	78	.957	88	1.322
69	.707	79	.989	89	1.364

ANALYSIS OF LIMESTONES, MAGNESITES, DOLOMITES, AND MATERIALS DERIVED FROM THEM.

SILICA.

METHOD WHEN SAMPLE IS NOT SOLUBLE IN HYDROCHLORIC ACID.

A 5 gram sample is mixed with 2.5 grams of sodium carbonate in a platinum crucible and sintered for 20 to 30 minutes in a muffle furnace or strong blast flame. The sintered cake is dissolved in water and hydrochloric acid, and the solution is evaporated to dryness. The subsequent treatment is the same as for the determination of silica in blast furnace slags. A second evaporation is seldom made when the silica content is under 3 per cent. If the percentage of magnesia is high, the baking temperature is kept close to, but under, 110° C., inasmuch as a higher temperature is conducive to the formation of magnesium silicate which is soluble in dilute hydrochloric acid.

METHOD WHEN SAMPLE IS SOLUBLE IN HYDROCHLORIC ACID.

In the analysis of material that is readily decomposed by hydrochloric acid, time may be saved by direct solution of the sample. One gram of the sample is transferred to a porcelain dish provided with a cover glass, moistened with water, and dissolved in 20 cc. of hydrochloric acid (1:1). Heat is applied if necessary. After the material is decomposed, the lid is removed from the dish, and the solution is evaporated to dryness. The operation from this point is the same as for silica in blast furnace slags.

ALUMINA, TITANIA, IRON, AND MANGANESE.

The analysis for these constituents is conducted as outlined under blast furnace slags. Two precipitations of the alumina, titania and iron should be made in the analysis of magnesite and calcined dolomite.

LIME.

The analysis for lime is made by the same methods with two exceptions as for lime in blast furnace slags. In the analysis of materials with a high magnesia content, particularly in the case of magnesite or calcined dolomite, a double precipitation of the lime must be made. If the percentage of lime is high, as in limestone, calcined dolomite, and burned lime, an aliquot part, corresponding to approximately .5 gram of calcium oxide, of the filtrate reserved for the determination of lime is taken for the analysis.

The short methods for lime are also used. If only lime and magnesia are to be determined on a sample, one gram of the material is sintered with sodium carbonate as for the determination of silica. The sintered mass is dissolved in hydrochloric acid (1:1), the solution is neutralized with ammonia, and 10 cc. of ammonia in excess are added. The solution is boiled a few minutes, when the lime is precipitated in the presence of silica and the hydroxides of iron and aluminum, and determined by titration in the usual way.

MAGNESIA.

For the determination of magnesia in these materials, the method described for the determination of magnesia in blast furnace slags is employed with the observance of two precautions. If the content of magnesia is high, one-half or one-fourth of the filtrate from the lime is taken; and, if an excessive amount of ammonium salts have accumulated from preceding determinations, these are eliminated by evaporation and volatilization.

SULPHUR.

Five grams of the sample are sintered as for the determination of silica, and the sintered cake is dissolved in hydrochloric acid (1:1), a slight excess being employed. The sulphur is precipitated in the hot solution with barium chloride solution as in the determination of sulphur in weathered blast furnace slags.

PHOSPHORUS.

Two to five grams of the sample are sintered with sodium carbonate, and the silica is separated as in the determination of that constituent with the exception that the residue from the evaporation and baking is digested with 25 cc. nitric acid (sp. gr. 1.20) instead of hydrochloric acid. The undissolved portion is removed by filtration, the filtrate and washings are heated to boiling, and the phosphorus is precipitated and determined as described in the method for phosphorus in miscellaneous slags.

CARBON DIOXIDE.

Carbon dioxide in raw material is determined by evolving the gas by means of hydrochloric acid and absorbing it, after purification, in a suitable weighing bottle. The evolution flask for this purpose is equipped with a two-hole rubber stopper by which a globe-shaped separatory funnel and a reflux condenser are attached. The absorption train, which is connected to

the condenser, is composed of a tube containing anhydrous calcium chloride a tube containing anhydrous copper sulphate, and a weighing bottle containing soda asbestos or soda lime and phosphorus pentoxide, in the order named. The train is aspirated by means of suction. The incoming air is freed from carbon dioxide by passage through soda lime contained in a small tube which is connected to the separatory funnel with a stopper.

For the determination, one to five grams of the sample are transferred to the evolution flask. The apparatus, without the weighing bottle, is connected, and a current of purified air is swept through it. The suction is now cut off, the separatory funnel, with stopcock closed, is nearly filled with hydrochloric acid (1:1), and the weighed absorption bottle is inserted in place. With all the apparatus connected, the acid is permitted to flow slowly upon the sample in the flask at a rate that evolves the gas not too rapidly for absorption. A few cubic centimeters of the acid are retained in the funnel to serve as a seal.

When the violent action is over, the solution in the flask is gradually heated to boiling and boiled for 2 to 3 minutes. The stopcock in the separatory funnel is now opened, admitting the balance of the acid to the flask, whereupon suction is gradually applied until a fairly brisk bubbling is obtained. This is continued until the residual carbon dioxide is all drawn into the weighing bottle, the incoming air being purified by passage through the soda lime tube. The increase in weight of the absorption bottle is carbon dioxide. This, multiplied by 100 and divided by the weight of the sample taken, gives the per cent of carbon dioxide in the sample.

Carbon dioxide, in calcined materials that are free from carbonaceous impurities, is determined by igniting one gram of the sample in a combustion furnace in a current of oxygen, similar to the determination of carbon in steel, as described in the Sampling and Analysis of Ferro-Alloys by the Chemists of the United States Steel Corporation.

COMBINED WATER.

Combined water of calcined materials is determined on a suitable weight of the sample by igniting in a combustion furnace in a stream of oxygen or air which has been dried over phosphorus pentoxide. The evolved water is collected in a weighing tube of phosphorus pentoxide which is attached to the outlet end of the combustion tube. The increase in weight of the phosphorus pentoxide weighing tube represents the combined water in the sample.

LOSS ON IGNITION.

One gram of the sample is transferred to a tared platinum crucible. The crucible is covered with its lid, placed in the front part of a muffle furnace which is heated to a temperature of 1000°C., and gradually moved to the hot zone, when the lid is removed. The crucible and contents are ignited one hour, removed from the furnace, cooled, and weighed. They are returned to the furnace, ignited fifteen minutes, and again weighed. This operation is repeated until constant weight is obtained. The loss in weight multiplied by 100 equals the per cent of loss on ignition.

If carbonaceous matter, ferrous compounds, or other oxidizable substances are not present in the sample, the per cent of loss on ignition is very close to the amount of carbon dioxide plus combined water and may be thus reported if a separate determination of each component is not required.

ANALYSIS OF FLUOR SPAR.

SILICA.

One-half gram of the finely ground sample is transferred to a 200 cc. beaker, and 10 cc. of 10 per cent acetic acid are added. The beaker is covered with a cover glass, and the sample is digested on a water bath for one hour with occasional shaking. The cover glass is removed, and the contents of the beaker are evaporated to dryness and baked on a water bath for thirty minutes. Fifty cubic centimeters of water are added, when heat is applied until the contents of the beaker are boiling, thereby precipitating the iron which has dissolved in the acetic acid. The residue is collected on a paper and washed well with hot water. The filtrate contains the calcium carbonate and magnesium carbonate of the sample. It is reserved for the determination of these components. The paper and residue are transferred to a large platinum crucible and ignited. The crucible and contents are weighed. The residue is crushed with a platinum rod or any other suitable instrument. Two cubic centimeters of strong hydrofluoric acid are added, and the contents of the crucible are evaporated to dryness. This treatment is repeated. The residue is now just moistened with hydrofluoric acid, and a small amount of ashless paper pulp is introduced to promote the formation of a powdery residue. Ammonia is cautiously added until the acid is neutralized and the iron is precipitated. After evaporation to dryness, the crucible and contents are ignited and weighed. The loss in weight multiplied by 200 gives the per cent of silica in the sample.

ELIMINATION OF FLUORINE AND DECOMPOSITION OF SAMPLE.

The residue remaining in the crucible after the volatilization of the silica is broken up as much as possible and moistened with two cubic centimeters of concentrated sulphuric acid. The excess sulphuric acid and the hydrofluoric acid formed are expelled by carefully heating the crucible over a circular gas burner until the fumes have ceased to appear. The evaporation is repeated with one cubic centimeter of sulphuric acid, when the crucible and residue are ignited at a high temperature over a Meker burner. It is essential that all traces of fluorine be eliminated by this operation, otherwise calcium will be precipitated as the fluoride when ammonia is introduced in the subsequent operations. The residue in the crucible is fused with a small amount of sodium carbonate, and the fusion is dissolved in water and hydrochloric acid, employing 10 cc. of acid in excess. The procedure at this point is varied, depending on whether or not lead and zinc are present.

LEAD SULPHIDE.

If the sample contains lead, the solution is boiled to expel carbon dioxide when it is made alkaline with ammonia. Five to ten cubic centimeters of

colorless ammonium sulphide made by passing hydrogen sulphide at a moderate rate of flow into 100 cc. of 1:1 ammonium hydroxide for twenty minutes) are carefully added, and the boiling is continued for several minutes. The precipitate, which may contain lead, iron, aluminum, and zinc, is permitted to settle and is collected on a small filter. The paper and precipitate are washed with water containing 5 cc. of colorless ammonium sulphide per 100 cc. and transferred to the beaker in which the precipitation was made. Twenty cubic centimeters of nitric acid (sp. gr. 1.20) are introduced, and the contents of the beaker are digested at a temperature below boiling until the precipitate is in solution. Over-heating at this point may oxidize the lead sulphide to sulphate in which form it is partially insoluble. The contents of the beaker are filtered, the filtrate being received in a 250 cc. beaker, 15 cc. of sulphuric acid (1:1) are added, and the solution is evaporated to copious evolution of sulphur trioxide fumes. A brown coloration in the solution at this point is due to the oxidation of particles of filter paper and is destroyed by the addition, carefully, of a few crystals of sodium chlorate. The beaker and contents are cooled, the solution is cautiously diluted to about 150 cc. with water, and the beaker is allowed to stand in a cold water bath for three hours with frequent stirring of the contents.

The lead sulphate, which separates, is collected on a close-textured tared paper, which has been dried for one hour at 105°C., and washed with 5 per cent sulphuric acid. The beaker in which the filtrate has been received is replaced by an empty container. The paper and precipitate are thoroughly washed with a ten per cent solution of ethyl alcohol to remove the acid, dried, and weighed. The weight of lead sulphate is multiplied by the factor 78.90 and 2 to find the percentage of lead sulphide in the sample.

IRON AND ALUMINUM OXIDES.

To the filtrate from the lead sulphate, 3 cc. of nitric acid are added. The solution is heated to boiling, and the iron and aluminum are precipitated with ammonia, added in slight excess. The hydrates are collected on a paper, washed, ignited, and weighed. The per cent of the oxides of iron and aluminum is reported.

ZINC SULPHIDE.

The filtrate remaining from the preceding operation, after 5 cc. of a 10 per cent solution of ammonium phosphate has been added, is boiled to expel the excess of ammonia. Zinc, if present, will be completely precipitated as the phosphate when the neutral point is reached. It is collected and

washed on a paper, ignited in a porcelain or an alundum crucible, slowly at first and finally at the highest temperature of the muffle furnace, and weighed. The weight of zinc pyrophosphate, multiplied by the factor 63.93 and 2, gives the percentage of zinc sulphide in the sample.

IRON AND ALUMINUM OXIDES WHEN LEAD AND ZINC ARE NOT PRESENT.

To the solution of the sodium carbonate fusion, two cubic centimeters of concentrated nitric acid are added, when it is heated to boiling. Ammonia is added until in a slight excess. The solution is diluted to 300 cc. and boiled one minute. The precipitates of iron and aluminum hydroxides are removed by filtration, ignited in a platinum crucible, and weighed. The per cent of iron and aluminum oxides is reported.

CALCIUM FLUORIDE.

The filtrate from the ammonium sulphide separation is acidified with hydrochloric acid and boiled to expel the hydrogen sulphide. It is then made ammoniacal, when it is ready for the precipitation of the lime. To this solution, or to the filtrate remaining from the ammoniacal separation of the iron and aluminum, 40 cc. of a saturated solution of ammonium oxalate are added. The solution is heated to boiling, when 10 cc. of ammonium hydroxide are added, drop by drop, with stirring. Boiling and stirring is continued for 10 minutes, whereupon the precipitate is allowed to settle, collected on a filter, washed, and titrated with standard potassium permanganate solution as described for the determination of lime in blast furnace slags. The per cent of calcium oxide is multiplied by the factor 1.3924 to obtain the per cent of calcium fluoride.

MAGNESIUM FLUORIDE.

To the cold filtrate from the calcium fluoride determination, 5 cc. of 10 per cent ammonium phosphate solution are added, followed by 10 cc. of ammonia. The solution is permitted to stand for a few hours, when any ammonium magnesium phosphate precipitate is removed by filtration and ignited to magnesium pyrophosphate. The weight of magnesium pyrophosphate, multiplied by the factor 55.96 and 2, gives the percentage of magnesium fluoride in the sample.

CALCIUM CARBONATE AND MAGNESIUM CARBONATE.

The filtrate from the acetic acid extraction is heated to boiling, when 2 cc. of concentrated nitric acid are added. The solution is made slightly ammoniacal and boiled. Any iron or aluminum, which precipitates, is removed by filtration, ignited, and weighed. The amount is added to the principal weight of the oxides of iron and aluminum, which is found by another operation.

The calcium in the filtrate is precipitated with ammonium oxalate and ammonia, and the amount of calcium oxide is determined by the gravimetric method for lime in blast furnace slags. The calcium oxide found is converted to the calcium carbonate by the factor 1.7848. The magnesium is determined as described in the preceding method for magnesium fluoride, and the magnesium pyrophosphate is multiplied by .7572 to obtain the amount of magnesium carbonate.

CARBON DIOXIDE.

Carbon dioxide is determined by igniting one gram of the sample in a combustion furnace in a current of pure oxygen, similar to the determination of carbon in steel, as described in Sampling and Analysis of Ferro-Alloys by the Chemists of the United States Steel Corporation. The carbon dioxide, absorbed by soda lime or soda asbestos in a suitable bottle, is weighed as such, and the percentage is obtained by multiplying the weight in grams by 100.

SULPHUR.

One gram of the sample is fused with a mixture of ten parts sodium carbonate and one part sodium nitrate, and the fusion is leached with water. The solution is boiled a few minutes and filtered from the insoluble portion. The filtrate is made slightly acid with hydrochloric acid and heated to boiling, whereupon the sulphur is precipitated as barium sulphate by the addition of barium chloride solution, drop by drop, with stirring. The analysis is concluded as described in the method for total sulphur in blast furnace slags.

ALKALIES.

These components of fluor spar are determined as described in the method for alkalies under the analysis of clay, fire brick, and bauxite.

VALUATION OF FLUOR SPAR.*

CALCIUM FLUORIDE, SILICA, AND CALCIUM CARBONATE.

One gram of the finely-powdered sample is placed in a small flask, and 10 cc. of ten per cent acetic acid are added. The flask is covered with a short-stemmed glass funnel and heated on a water bath for one hour, agitating from time to time. The funnel is removed, and the contents of the flask are evaporated to dryness. Fifty cubic centimeters of water are introduced, and the contents of the flask are heated to boiling, whereupon the iron, which was dissolved by the acetic acid, is precipitated as the basic acetate. The insoluble residue is collected on a paper, washed well with warm water, and ignited at a temperature as low as possible in a weighed platinum crucible. The loss in weight minus .0010 gram (the amount of calcium fluoride soluble in acetic acid under the conditions specified) is calcium carbonate.

Approximately one gram of yellow mercuric oxide in the form of an emulsion in water is added to the pulverized residue in the platinum crucible. The contents of the crucible are evaporated to dryness and carefully ignited at a temperature sufficient to volatilize the mercuric oxide. The crucible is cooled and weighed. About 2 cc. of hydrofluoric acid are added and the contents of the crucible are evaporated to dryness. The operation is repeated two times, using one cubic centimeter of hydrofluoric acid. A few drops of hydrofluoric acid are added, followed by some macerated filter paper and a few drops of ammonium hydroxide to precipitate the iron. The contents of the crucible are evaporated to dryness, when the crucible and contents are ignited at the same temperature as before and weighed. The loss in weight is silica.

Two cubic centimeters of hydrofluoric acid and ten drops of concentrated nitric acid are added. The crucible is covered with its lid and placed on a moderately warm water bath, where it is permitted to remain for thirty minutes. The lid is removed, and the contents of the crucible are evaporated to dryness. Another two cubic centimeters of hydrofluoric acid are introduced and evaporated. If the contents of the crucible are not entirely white, evaporation with hydrofluoric acid is repeated. A few drops of hydrofluoric acid

*This method for the valuation of fluor spar by the determination of calcium fluoride, silica, and calcium carbonate was published by Dr. E. A. Bidtel, in the Journal of Industrial and Engineering Chemistry, Volume 4 (1912), Number 3 and Volume 6 (1914), Number 3.

and 10 cc. of ammonium acetate extraction solution are added, and the residue in the crucible is digested on a boiling water bath for thirty minutes. The solution is filtered, and the residue is washed by decantation with hot water containing 5 cc. of ammonium acetate extraction solution per 100 cc. and finally with pure hot water. The paper and residue are ignited in the same crucible, and the residue, which should be entirely white, is weighed as pure calcium fluoride. This weight plus .0010 gram (the amount of calcium fluoride dissolved by the acetic acid extraction) gives the total calcium fluoride in the sample.

The purity of the calcium fluoride may be tested as follows: It is broken in the crucible as finely as possible. Two cubic centimeters of concentrated sulphuric acid are added, heat is applied to decompose the calcium fluoride, and the excess sulphuric acid is evaporated. The evaporation is repeated, using one cubic centimeter of sulphuric acid. The calcium sulphate is ignited, weighed, and calculated to calcium fluoride by the factor .5735. This should be the same as the amount of calcium fluoride that was found by weighing. Approximately five grams of sodium carbonate are added to the crucible and mixed with the calcium sulphate. The mixture is fused, and the fusion is dissolved in hydrochloric acid, using a slight excess. A white precipitate at this point indicates the presence of barium. The amount may be determined, if desired, by collecting the precipitate of barium sulphate on a paper, igniting, and weighing.

SOLUTION USED.

Ammonium Acetate Extraction Solution.

Four hundred cubic centimeters of acetic acid (80%) are transferred to a liter flask and carefully neutralized with concentrated ammonia. Twenty grams of citric acid are added, and, when the acid has dissolved, the flask is filled to the mark with concentrated ammonia.

LEAD SULPHIDE, IRON AND ALUMINUM OXIDES, AND ZINC SULPHIDE.

These constituents may be determined in the filtrate which is obtained when the impurities are extracted from the calcium fluoride. This filtrate is heated to boiling, 5 to 10 cc. of colorless ammonium sulphide are carefully added, and the solution is boiled a few minutes. The precipitate is removed by filtration and used for the determination of lead sulphide, iron and aluminum oxides, and zinc sulphide, as described for these components in the preceding methods for the analysis of fluor spar. Allowance should be made in the calculations for an initial weight of one gram of the sample.

ANALYSIS OF CLAYS, FIRE BRICK, AND BAUXITE.

SILICA.

One-half to one gram of the material is fused with 5 to 10 parts of sodium carbonate, and any particles that fail to dissolve in hydrochloric acid (1:1) are removed by filtration and fused with potassium bisulphate. The second fusion is dissolved in hydrochloric acid, and the solution is added to that of the initial fusion. In the case of calcined materials of high alumina content and all materials containing an appreciable amount of titania, the sample is fused direct with 5 to 10 parts of fused potassium bisulphate. The melt is dissolved in water and hydrochloric acid. The solution of the sample, in either case, is evaporated to dryness, and the silica is determined in the same manner as prescribed for the determination of silica in blast furnace slags. If the content of silica is over 30 per cent, a second evaporation and separation of silica should be made. The residue, remaining in the crucible after the volatilization of the silica, is fused with a small amount of sodium carbonate, and the fusion is added to the filtrate from the silica determination.

ALUMINA.

The filtrate from the silica separation is heated to boiling, 5 cc. of concentrated nitric acid are added, and the aluminum, iron, titanium, and phosphorus are precipitated with ammonia, added in slight excess. This precipitate is collected on a filter and washed three times, when the paper and precipitate are transferred to the beaker in which the precipitation was originally made. The paper is macerated with a glass rod, and sufficient hydrochloric acid (1:1) is added to dissolve the precipitate. The solution is diluted to approximately 100 cc., and the precipitation with ammonia is repeated. This precipitate, after filtration and washing, is slowly ignited in a platinum crucible. The presence of paper pulp facilitates the filtration and washing, and effects the formation of a powder on ignition of the precipitate that is readily soluble in acid for the determination of iron. The weight obtained represents the oxides of aluminum, iron, titanium, and phosphorus. The amount of alumina is found by deducting from the total oxides the oxides of iron, titanium, and phosphorus, which are determined individually by the methods subsequently described.

IRON.

The oxides of aluminum, iron, titanium, and phosphorus are transferred to a small beaker and dissolved in a minimum amount of concentrated hydrochloric acid. The iron is reduced with stannous chloride solution, and the determination is finished as described in the method for iron in the analysis of blast furnace slags.

MANGANESE.

The filtrate from the ammoniacal separation of aluminum, iron, titanium, and phosphorus is reduced to a volume of 100 cc., or less, by evaporation. Approximately one gram of ammonium persulphate are added, followed by 10 cc. of ammonia. The solution is boiled for several minutes, when the manganese dioxide is collected on a paper and washed. It is dissolved with hot hydrochloric acid (1:1) and sulphurous acid, as described under manganese in blast furnace slags, and the determination is finished by the persulphate-arsenite method.

LIME.

Five cubic centimeters of a solution of ammonium oxalate are added to the filtrate from the manganese separation, and the solution is evaporated to a low volume to insure the precipitation of the small amount of lime. A few drops of ammonia are now added, whereupon the lime is collected on a filter and determined by the gravimetric method as described under blast furnace slags.

MAGNESIA.

The filtrate from the determination of lime is evaporated to dryness in a porcelain dish, when the ammonium salts are expelled by heating. The residue is dissolved in approximately 100 cc. of water. Five cubic centimeters of a ten per cent ammonium phosphate solution are added to the solution, followed by 10 cc. of concentrated ammonia. The solution is stirred and permitted to stand a few hours. The determination is concluded as described for magnesia in blast furnace slags.

TITANIA.

The titania is determined on one gram of the sample by the short method as described for titania in blast furnace slags.

PHOSPHORUS.

The filtrate that is obtained upon the separation of sodium titanate in the preceding method contains all the phosphorus. It is acidified with hydrochloric acid and evaporated to dryness, when the silica is separated by the usual operations. The resultant filtrate is reduced to a low volume by evaporation in order to eliminate the hydrochloric acid. The determination is then concluded by the method for phosphorus as outlined under miscellaneous slags.

ALKALIES.

One gram of the sample is thoroughly ground in an agate mortar with an equal weight of ammonium chloride and eight times its weight of calcium carbonate. The intimate mixture is transferred to a platinum crucible of 30 to 35 cc. capacity and covered with a rather heavy layer of calcium carbonate. The crucible with lid in place is protected by a suitable asbestos shield, so that only the lower two-fifths is subject to direct heating. Gentle heat is applied by means of a burner, until the odor of ammonia can no longer be detected; the bottom of the crucible is then maintained at a bright red heat for three-quarters of an hour. The contents of the crucible are removed to an agate mortar, from which, after being crushed, the powder is transferred to a platinum dish, the crucible and mortar being rinsed with hot water. Water is added to make a total volume of about 100 cc., when the residue is digested until thoroughly disintegrated, collected on a paper, and washed with hot water, the filtrate being received in another platinum dish. The lime is precipitated in the boiling solution by adding 10 cc. of a 20 per cent solution of ammonium carbonate containing 20 per cent of concentrated ammonium hydroxide. The solution is filtered into another platinum dish, evaporated to small bulk, and acidified with a few cubic centimeters of hydrochloric acid, when any sulphur present is precipitated by adding 2 drops of a 10 per cent solution of barium chloride to the boiling solution. The solution is filtered into a platinum dish, and to the boiling filtrate are added 2 cc. of the ammonium carbonate solution. The solution is boiled for a few minutes and filtered from the barium carbonate into another platinum dish, and the filtrate is evaporated to dryness. The dish and residue are carefully heated to expel ammonium salts. A few cubic centimeters of hot water are added, followed by ammonia until alkaline, and the small amount of lime remaining is separated with a few drops of ammonium oxalate solution.

The resulting filtrate, received in an untared platinum crucible of 30 to 35 cc. capacity, is evaporated to dryness, and the crucible is gently ignited. The residue is moistened with hydrochloric acid, the solution is evaporated to dryness, and the crucible and contents are ignited at a dull red heat to constant weight. The contents of the crucible are dissolved in hot water, the solution is filtered into a small porcelain dish, and the filter, containing a slight insoluble residue, is returned to the original crucible, which is again ignited and weighed. The difference in weight represents the combined weight of sodium and potassium chlorides.

A blank test is made under the same conditions as described in the regular method, the weight obtained being deducted from the combined weight of sodium and potassium chlorides.

The potassium and sodium may be determined either by the direct or the indirect method, as described in the method for the determination of alkalies in blast furnace slags.

COMBINED WATER.

Combined water is determined by the same method as described for combined water in limestones and dolomites.

EMPIRICAL FORMULA.

For the purpose of indicating the refractory qualities of fire clays or fire clay brick, the molecular ratios of the silica and of the fluxing oxides to the alumina are calculated and reported with the analysis. In detail, the percentage of each constituent is divided by its molecular weight, the iron being calculated to ferrous oxide, and the resulting molecular numbers are each divided by the number for the alumina. The sum of all the resulting quotients for metallic oxides, other than alumina, determines the class of the refractory, the numbers .22 and .32 being the upper limit, respectively, for the first and second grade when the number for the silica is 3 or less. The titania is not considered.

EXAMPLE.

Calculation of Refractory Value by the Empirical Formula.

Fire Clay.

	Sample No. 1		Sample No. 2	
Silica	49.16%	$\frac{49.16}{60.3} = .815$	46.69%	$\frac{46.69}{60.3} = .774$
Alumina	35.70	$\frac{35.70}{102.2} = .349$	35.65	$\frac{35.65}{102.2} = .349$
Lime	.28	$\frac{.28}{56} = .0050$	1.84	$\frac{1.84}{56} = .0329$
Magnesia	1.14	$\frac{1.14}{40} = .0285$	1.38	$\frac{1.38}{40} = .0345$
Alkalies	.00	$\frac{.00}{94.2} = .0000$	2.07	$\frac{2.07}{94.2} = .0220$
Ferrous Oxide	2.76	$\frac{2.76}{72} = .0383$	4.37	$\frac{4.37}{72} = .0607$
		.0718		.1501

$$\frac{.0718}{.349} = .206 \text{ RO} \qquad \frac{.1501}{.349} = .43 \text{ RO}$$

$$\frac{.349}{.349} = 1\ Al_2O_3 \qquad \frac{.349}{.349} = 1\ Al_2O_3$$

$$\frac{.815}{.349} = 2.34\ SiO_2 \qquad \frac{.774}{.349} = 2.22\ SiO_2$$

$.206\ RO \cdot 1\ Al_2O_3 \cdot 2.34\ SiO_2$ $\quad .43\ RO \quad 1\ Al_2O_3 \cdot 2.22\ SiO_2$

By these calculations, it is seen that sample No. 1 meets the chemical specification for a first grade fire clay, which is .22 RO, and that sample No. 2 is a third grade clay, its RO value .43 being above the limit of .32 RO, which is specified as the maximum for second grade material.

It must be emphasized, however, that these limits furnish a classification which is approximate and by no means absolute. For instance, if the RO value is just above or below the established limits, the clay or brick cannot definitely be classified as of any certain grade.

ANALYSIS OF GANISTER, SILICA BRICK, AND SANDS.

SILICA.

FUSION METHOD.

Silica is determined on one-half gram of the sample by the method for silica which is given under the analysis of clays, fire brick, and bauxite.

METHOD BY DIFFERENCE.

The sum of all constituents other than silica is subtracted from 100 per cent. The remainder is reported as the per cent of silica in the sample.

METHOD BY LOSS ON VOLATILIZATION.

This method for the determination of silica is applicable only when the calcium oxide content of the sample is .2 per cent or less, because of the error which is introduced by the fixation of sulphuric acid by calcium oxide. For the determination, one to two grams of the sample are treated in a platinum crucible with 15 cc. of hydrofluoric acid and 1 cc. of concentrated sulphuric acid. The contents of the crucible are evaporated to dryness, when the crucible and contents are ignited and weighed. The loss in weight represents silica. The residue is fused with sodium carbonate, the fusion is dissolved in hydrochloric acid (1:1), and the solution is evaporated to dryness. Any silica, which may not have been volatilized, is separated in the usual manner and determined. The weight is added to that obtained by volatilization, the sum being the total silica of the sample.

OTHER CONSTITUENTS.

The solution, remaining from the determination of silica by volatilization, is used for the determination of alumina, iron, manganese, lime, and magnesia. Even if the silica is not determined by the method by loss on volatilization, it is eliminated as described in this method before the other components are determined. The analysis is conducted by the same methods as outlined for the analysis of clays, fire brick, and bauxite, excepting the determination of alumina, when one precipitation of the aluminum, iron, titanium, and phosphorus with ammonia is sufficient. Titania, phosphorus, and alkalies are also determined by the methods given for clays, fire brick, and bauxite.

ANALYSIS OF CHROME ORE.

CHROMIC OXIDE.

One gram of the ore is fused in a porcelain or nickel crucible with 5 to 10 grams of sodium peroxide. The fusion is disintegrated with water in a beaker of 600 cc. capacity. Water is added to make a total volume of approximately 400 cc., followed by one-half gram of sodium peroxide. The contents of the beaker are boiled ten minutes. Sulphuric acid (1:1) is then cautiously added until there are 5 cc. in excess. Two cubic centimeters of hydrochloric acid (1:1) are introduced for the purpose of decomposing any permanganic acid which may be present, whereupon the solution is boiled until the free chlorine is expelled. The beaker and contents are cooled, the chromic acid is reduced with standard ferrous ammonium sulphate solution, an excess being added, and the excess is titrated with standard potassium permanganate or bichromate solution.

PERMANGANATE TITRATION.

Standard fifth normal potassium permanganate solution is added to the solution in the beaker until the first discernable pink is obtained. For the purpose of comparing the standard solution, an amount of the ferrous ammonium sulphate solution equal to the quantity employed to reduce the chromic acid is transferred to a suitable beaker, and 350 cc. of water are added. Potassium permanganate solution is now added until the first pink color is observed, and the number of cubic centimeters used is noted. The difference in cubic centimeters between the volume of permanganate solution required in the blank titration and that required in the actual determination, representing the volume of permanganate equivalent to the chromic oxide in the sample, is multiplied by the chromic oxide factor of the standard permanganate and 100 to obtain the percentage of chromic oxide.

SOLUTIONS USED.

N/5 Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate	78.4 grams
Sulphuric acid (1:1)	100 cc.
Water to make	1000 cc.

The salt is dissolved in the dilute acid in a 1000 cc. volumetric flask. When solution has been effected, the flask is filled to the mark with water.

N/5 Sodium Oxalate Solution.

Sodium oxalate.....13.4 grams
Water.....1000 cc.

N/5 Potassium Permanganate Solution.

Potassium permanganate.....6.32 grams
Water.....1000 cc.

The potassium permanganate is dissolved in boiling water, and the solution is permitted to stand for 24 hours. It is then filtered through an asbestos filter and standardized as follows: Fifty cubic centimeters of the standard sodium oxalate solution, accurately measured, are transferred to a beaker, and 350 cc. of water and 10 cc. of cold recently boiled sulphuric acid (1:1) are added. The permanganate solution is now added slowly with stirring until the end point is reached. The solution may be adjusted, if desired, to make it exactly one-fifth normal.

One cubic centimeter of fifth normal permanganate solution equals .005067 gram chromic oxide, but permanganate equal to six-tenths per cent of the chromic oxide is required to overcome the green color of the chromic salt in solution. Therefore, the factor of normality, multiplied by 5 and .0050974, gives the strength in chromic oxide of one cubic centimeter of the standard permanganate solution

BICHROMATE TITRATION.

Standard potassium bichromate solution is added to the solution in the beaker, while it is stirred vigorously, until a drop removed and placed upon a drop of potassium ferricyanide solution will not produce a blue color, thus showing the ferrous salt completely oxidized. An amount of ferrous ammonium sulphate solution, equal to the quantity used to afford an excess in reducing the chromic acid, is titrated in a like manner to obtain a comparison. From the equivalent in cubic centimeters of bichromate solution thus found is subtracted the number of cubic centimeters of bichromate solution required to titrate the excess of ferrous ammonium sulphate solution in the actual determination. The remainder is multiplied by the chromic oxide value of one cubic centimeter of the standard bichromate solution and 100 to find the percentage of chromic oxide in the sample.

SOLUTIONS USED.

Standard Ferrous Ammonium Sulphate Solution.

Ferrous ammonium sulphate..... 70 grams
Sulphuric acid (1:1)..... 100 cc.
Water to make.....1000 cc.

The solution is prepared as described under solutions in the preceding method.

Standard Potassium Bichromate Solution.

Potassium bichromate..... 8.9 grams
Water.....1000 cc.

The potassium bichromate solution is standardized by means of one gram of the Corporation Iron Ore Standard as described in the Iron Ore Pamphlet, its value in iron being thereby obtained. The iron value multiplied by the factor .4537 gives the value in chromic oxide of one cubic centimeter of the standard bichromate solution.

Potassium Ferricyanide Indicator Solution.

Potassium ferricyanide..... 1 gram
Water.....1000 cc.

This solution should be freshly prepared each day.

SILICA.

One-half gram of the sample is fused with five grams of sodium peroxide in a nickel crucible. The fusion is dissolved in water in a porcelain vessel and acidified strongly with hydrochloric acid. Ten cubic centimeters of alcohol are added to reduce the chromium, whereupon the silica is separated with two evaporations of the solution and determined as in the analysis of blast furnace slags. A blank determination is made, and a correction is applied for the amount of silica derived from the crucible and chemicals used.

LIME AND MAGNESIA.

Two basic acetate separations with intervening filtration are made on the filtrate from the determination of the silica. The procedure for basic acetate separations is described in the method for alumina-titania under miscellaneous slags and scales.

The combined filtrates from the acetate separations are employed for the determination of lime and magnesia. The manganese is separated as described in the method for manganese under miscellaneous slags and dis-

carded. The lime and magnesia are determined as outlined in the analysis of blast furnace slags, employing the method for lime which uses the filtrate from the ammonium hydrate separation. Inasmuch as the magnesia content of chrome ore is high, it is advisable to dissolve the first precipitate of magnesium phosphate with hydrochloric acid (1:1) and reprecipitate to purify from nickel and alkali salts.

ALUMINA-TITANIA.

The basic acetate precipitate obtained in the preceding method is dissolved with hydrochloric acid (1:1), the solution being received in the beaker wherein the precipitation was made. The alumina is then determined as the phosphate as explained in the phosphate method for alumina in blast furnace slags.

If the ore contains titanium, it will be retained on the filter as a part of the basic acetate precipitate. In this case, the acetate precipitate is dissolved, and the titanium is separated by precipitation with sodium thiosulphate prior to the determination of the alumina. The operations in detail are described in the method for the determination of alumina when titanium is present, which appears under miscellaneous slags, cinders, and scales. In addition, the residue, remaining in the crucible after the volatilization of the silica, should be rendered soluble by fusion with sodium carbonate and added to the solution before the basic acetate separation is made.

ALTERNATE METHOD FOR ALUMINA, LIME, AND MAGNESIA.

LIME AND MAGNESIA.

One-half gram of the ore is fused with sodium peroxide in a nickel or iron crucible. The fusion is leached with water, and, after the addition of one-half gram of sodium peroxide, the solution is boiled ten minutes. The residue is allowed to settle, and the liquid is decanted through a large filter in a ribbed funnel, whereupon the residue is washed by decantation, until the washings are free from chromate solution, and then transferred to the paper. The filtrate, which contains all the chromium, sulphur, and phosphorus, and part of the alumina and silica, is reserved for the recovery of the alumina.